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RESOLUTION IN PROGRAMMED TEMPERATURE
GAS CHROMATOGRAPHY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL
FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER
OF SCIENCE IN CHEMISTRY

DEPARTMENT OF CHEMISTRY

BY

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The undersigned hereby certify that they have
read and recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled

RESOLUTION IN PROGRAMMED TEMPERATURE
GAS CHROMATOGRAPHY

submitted by John F. Fryer, B. Sc. in partial fulfilment
of the requirements for the degree of Master of Science
in Chemistry.

ABSTRACT

An examination has been made of resolution in programmed temperature gas chromatography. If the resolution of two chromatographic peaks is defined as the ratio of their separation divided by their average base-width, then it has been shown theoretically that resolution may be expressed as follows:

$$R = \frac{F}{r} \left(\frac{T_A - T_B}{V_{T_R}} \right) \sqrt{\frac{N}{4}}$$

where F is the flow-rate of carrier gas, r the heating rate for the chromatographic analysis, T_A and T_B are the retention temperatures (i.e. column temperature at peak emergence) for the two compounds A and B, V_{T_R} is the average isothermal retention volume for the two compounds as measured at their respective retention temperatures and N is the number of theoretical plates in the column.

The resolution may be divided into two parts, one characteristic of the solute--solvent interaction and the chromatographic program and which has been designated as the "intrinsic resolution", R_i , and the other dependent on the number of plates in the column. Thus

$$R = R_i \left(\sqrt{N/4} \right).$$

The relation of intrinsic resolution to retention characteristics and program has been examined. It has been found that for pairs selected from many different types of compounds the relationship of intrinsic resolution to program as expressed by F/r is of the same general shape. Intrinsic resolution reaches a relatively constant value with increasing F/r ratio at a value of F/r of about ten for most pairs of compounds.

Conditions for maximum resolution in programmed temperature gas chromatography have been suggested. These conditions are: flow-rate near

the optimum where N is a maximum and heating at a maximum limited only by keeping the F/r ratio greater than ten. The time for an analysis may be shortened with minimum loss of resolution by increasing both flow-rate and heating rate.

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INTRODUCTION

A separation by chromatography is based on the partition of a substance between two phases - one stationary, the other moving. The substance is eluted by the moving phase at a velocity dependent on the partition coefficient. These phases may be gas-liquid, gas-solid, liquid-liquid, or liquid-solid. The general term gas chromatography applies to separation by partition between gas and liquid or gas and solid.

Gas chromatography has been a rapidly expanding field of endeavour since 1952 when James and Martin (30) published an article dealing with the separation and estimation of volatile acids by gas-liquid partition chromatography. In an earlier paper published in 1941 dealing with liquid-liquid partition chromatography, Martin and Synge (41) had suggested the use of gas-liquid chromatography for analytical separations but in the interval no one took up their suggestion.

Gas chromatographic separations have in the past been carried out mainly under isothermal conditions. Techniques for the quantitative analysis of components have been fairly well standardized and many data are available in the literature. A somewhat newer technique, programmed temperature gas chromatography, involves a continually rising column temperature during the course of the chromatographic separation. Adequate theories have been worked out for retention temperatures and retention volumes in programmed temperature gas chromatography but up to now no satisfactory theory has been advanced related to the resolution (relative separation) of components. In this thesis an examination has been made of the factors involved. It was not found possible to give a completely general theoretical development and therefore a number of typical cases have been chosen to cover the whole range of practical interest. A number of practical separations have also been examined.

Also included are three appendices dealing with related aspects of programmed temperature chromatography which required investigation during the course of the work. These topics, which are of considerable practical interest to persons wishing to undertake programmed temperature chromatography and which have not been adequately dealt with in the literature are the effect of column dead-space on the calculation of retention temperatures and resolution; the relationship between fractional band impurity and resolution; and methods for the analytical evaluation of the integral relating retention temperatures and program.

REVIEW OF LITERATURE

A. THEORY OF ISOTHERMAL GAS CHROMATOGRAPHY

Retention Volume and Distribution Coefficient

A theory of chromatography relating the volume of fluid required to develop a chromatogram to the distribution coefficient was given by Martin and Synge (41) in 1941. The theory involves the concept of the theoretical plate--i.e. that a continuous column can be divided into a number of layers in each of which an equilibrium between the stationary and moving phases is established. The theoretical plate is defined as the thickness of layer such that the concentration of solute in the mobile phase issuing from it is in equilibrium with the mean concentration of solute in the stationary phase throughout the layer. Since the definition of plate involves the mean concentration it takes account of non-equilibrium of the moving phase with the concentration of solute at the exit of the plate. One may think of the mobile phase as moving in pulses one plateful at a time. Two simplifying assumptions were made: firstly, that diffusion from one plate to another is negligible and secondly, that the distribution coefficient of the solute between the two phases is independent of the absolute concentration of the solute or of other solutes.

By means of the binomial theorem, the following expression for the amount of solute in a particular plate was developed:

$$Q_{r+1} = \frac{1}{\sqrt{2\pi}r} (V/rv)^r \exp(r - V/v) \quad (1)$$

where

r = serial number of the plate
 Q_{r+1} = amount of solute in the $r + 1$ plate

v = effective volume of the plate = $H(A_m + K A_s)$
 H = height of plate
 V = volume of mobile phase used to elute the center of the solute band to the r^{th} plate
 A_m = cross-sectional area of mobile phase
 A_s = cross-sectional area of stationary phase
 K = distribution coefficient = $\frac{\text{Amount of solute per unit volume of stat. phase}}{\text{Amount of solute per unit volume of Mobile phase}}$

If

L = length of column, then
 N = total number of theoretical plates = L/H .

When the centre of the solute band reaches the end of the column, i.e.

when $r = N$,

$$Q_{r+1} = 1/\sqrt{2\pi r} = 1/\sqrt{2\pi N}$$

When r is large (greater than 100) the binomial curve becomes identical with the normal curve of error (Gaussian distribution)

$$Q = Q_{\text{max.}} e^{(-1/2 t^2)},$$

where t is the standard deviation. The advantage of the Gaussian curve is that it is much more amenable to mathematical calculation. A plot using equation 1 for $r = 100$ of Q against V/v is shown in figure 1. It has been reproduced from (41).

The treatment of van Deemter et al. (48) gives rise to a Poisson distribution which also at high values of N becomes the Gaussian curve. (See 34 for additional references).

The retention volume is defined as the volume of carrier gas which has entered the column when the center of the solute band is just leaving the column. That is, the retention volume is V for the N^{th} plate. From the definitions given above

$$\text{Retention Volume} = V = N v = \frac{L}{H} (A_m + K A_s) = V_{d.s.} + K V_s \quad (2)$$

where $V_{d.s.}$ is the volume of the column dead-space and V_s is the volume of stationary phase.

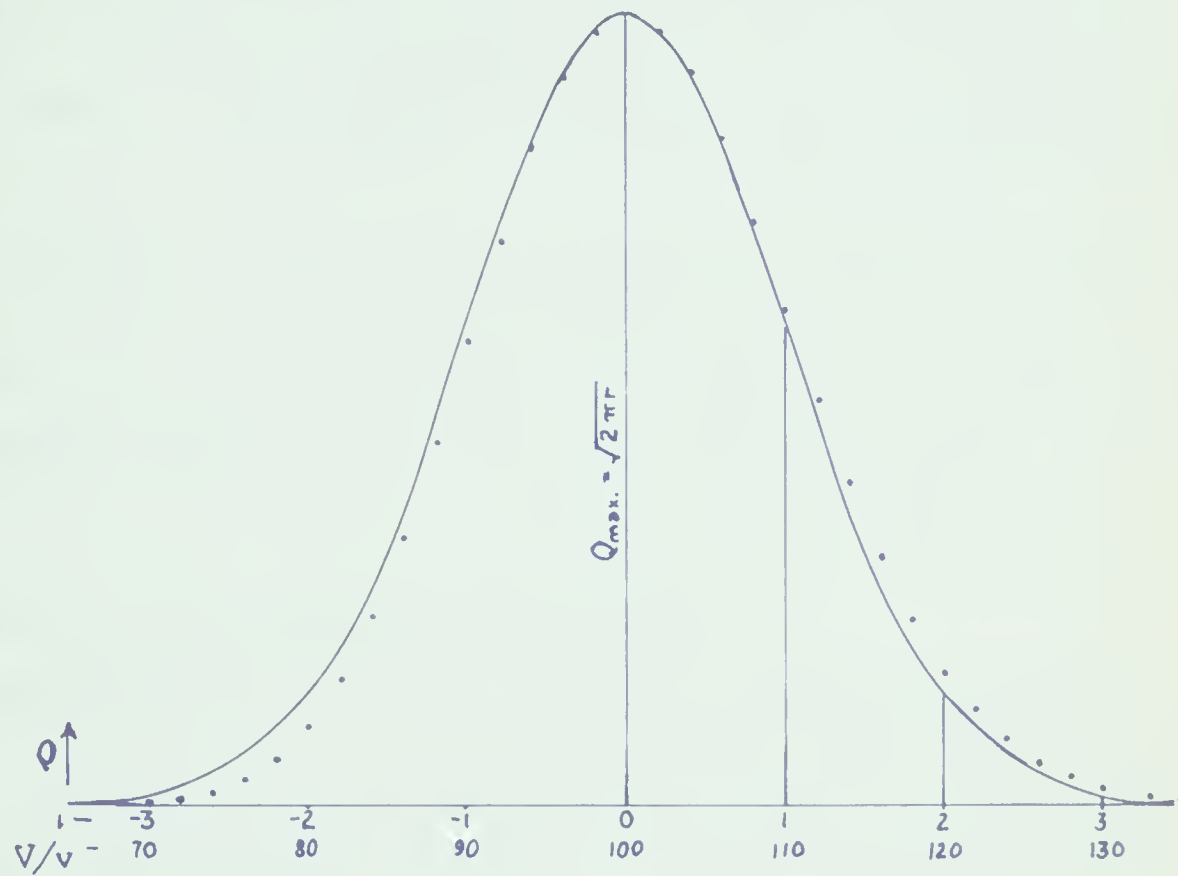


Fig. 1

The points represent the relation between V/v and Q for $r = 100$. The equation (2). The line is the normal curve of error with mean t , i.e. $Q_{max} = \sqrt{2\pi}r$.

A modification to the theory was made by James and Martin (30) to allow for the compressibility of the mobile phase. A compressible mobile phase increases in velocity from inlet to outlet of a column because of the decreasing pressure. The expression developed was:

$$\frac{V}{V_0} = \frac{2}{3} ((p_i/p_o)^3 - 1)/((p_i - p_o)^2 - 1) \quad (3)$$

where V_0 is the limiting retention volume when there is no pressure drop across the column, p_i is the inlet pressure to the column and p_o is the outlet pressure. Hereinafter V will refer to the limiting retention volume.

As would be expected, it is found experimentally that at constant temperature the retention volume of a solute will be constant for a particular solute-solvent system. The basis for separations of different solutes is then different partition coefficients between the two phases which result in different retention volumes.

Experimentally, it has been found that when $\log (V - V_{d.s.})$ is plotted against reciprocal temperature a straight line is obtained. (See 39 and 44) The partition coefficient to which retention volume is proportional, is related to the heat of solution of the solute in the solvent by the equation

$$K = A' \exp. (\Delta H/RT)$$

The heat of solution is therefore proportional to the slope of the $\log (V_R - V_{d.s.})$ --reciprocal temperature line.

Peak Width and Number of Theoretical Plates

Each chromatographic band or peak can be presented as a plot of solute concentration in the carrier gas leaving the column against time or the total volume of carrier gas. These curves are very close to

Gaussian or standard error curves. The width of a chromatographic peak can be characterized by the standard deviation of an error curve and the method most used in gas chromatography for finding the number of theoretical plates in a column from the normal error curve involves measuring the distance between the base-line intercepts of the tangents to the curve at the inflection points. These intercepts are located two standard deviations on each side of centre. As has been shown by Martin and Synge (41), one standard deviation represents \sqrt{N} where N is the number of plates. The ratio of the time, t , taken for the centre of the zone to emerge (measured from the time of injection of the solute) to the time taken for the portion of the zone two standard deviations on each side of the centre, w , is equal to $N/4 \sqrt{N}$. Therefore, (see figure 2)

$$N = 16 t^2 / w^2$$

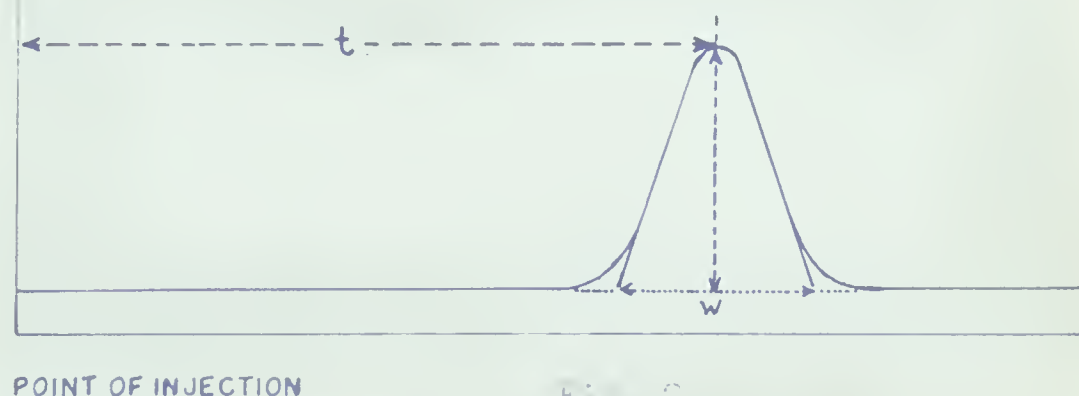


FIG. 2

For programmed temperature chromatography, Harrison et al. (29) suggested for the number of plates, what is effectively the same expression as that for isothermal gas chromatography, viz:

$$N = 16 \left(\frac{\text{Volume of gas to peak maximum}}{\text{flow rate at peak maximum}} \cdot \frac{\text{chart speed}}{\text{base width}} \right)^2$$

This formula gives rise to values of N which increase steadily with increasing retention volume - a totally unreasonable situation.

Habgood and Harris (26) pointed out that (assuming N is independent of temperature) the solute band in programmed temperature gas chromatography would be expected to spread through the same number of plates,

ΔN , by the time it reached the end of the column as it would in isothermal chromatography. Thus the correct general relationship is

$$N = 16 (N/\Delta N)^2 \quad (4)$$

and a correct interpretation of this in terms of gas volumes in programmed temperature gas chromatography is

$$N = 16 \left(\frac{V_{TR}}{\Delta V} \right)^2 \quad (5)$$

where V_{TR} is the retention volume which would be found for isothermal elution at retention temperature and ΔV is retention volume corresponding to peak width. The common chromatographic expression as used by Harrison is correct only for isothermal chromatography.

Van Deemter, Zuiderweg and Klinkenberg (48) have related the height of a theoretical plate, H, (i.e. the length of the column divided by the number of theoretical plates) to three factors.

Their equation may be given as $H = A + B/u + Cu$ where u is the linear velocity of the carrier gas and A is a constant arising from eddy diffusion in the column, B/u is the contribution of longitudinal diffusion of the solute in the mobile phase and Cu is the effect due to the resistance in the liquid phase to mass transfer of the solute between phases.

The equation is that of a hyperbola with minimum $A + 2(BC)^{1/2}$ at $u = B/C^{1/2}$. At low carrier gas velocities H is governed by B, while at high velocity C is the controlling factor. This means that there is one velocity for each carrier gas at which the column is operating at maximum

efficiency. It must be noted that u varies along the column due to compressibility of the mobile phase and, therefore, all sections of the column will not be operating at equal efficiency.

The factors contributing to H are apparent from the complete A, B, and C terms of the van Deemter equation. The eddy diffusion term, $A = 2 \lambda d_p$, where λ characterizes the manner in which the particles are packed and d_p is the average particle diameter, is independent of solute, solvent or operating conditions. The molecular diffusion term is $B = \gamma D_{\text{gas}}$, where D_{gas} is the diffusivity of the solute molecules in the carrier gas and γ is a correction factor for the tortuosity of the gas channels which counteracts the molecular diffusion to a certain extent. The resistance to mass transfer term, which is assumed to be entirely in the liquid phase, is

$$C = \frac{8}{\pi^2} \frac{K'}{(1+K')^2} \cdot \frac{d_f^2}{D_{\text{liq}}} \quad (6)$$

where $K' = K(F_{\text{liq}}/F_{\text{gas}})$, and K is the distribution coefficient of the solute, F_{liq} and F_{gas} are the fractions of cross section occupied by liquid and gas phase respectively, D_{liq} is the diffusivity of the solute molecules in the liquid phase and d_f is the effective thickness of the liquid phase on the particles of solid support.

A number of modifications of the basic van Deemter equation have been suggested by other workers (16, 19, 37, 38, and 46). An additional term, D_u , for resistance to mass transfer in the layer of stagnant gas surrounding the liquid has been suggested by Khan (37) as having the form

$$\frac{2}{3} \frac{\frac{F_{\text{liq}}}{F_{\text{gas}}} \cdot \frac{k_1}{k_2} \cdot d_{f1}^2}{\left[1 + \frac{F_{\text{liq}}}{F_{\text{gas}}} \cdot \frac{k_1}{k_2} \right]^2 D_{\text{gas}}} u \quad (7)$$

where d_{f1} is the "effective depth" of the gas phase, k_1 and k_2 are the absorption and desorption rate-constants respectively. A somewhat similar expression has been suggested by Kieselbach (38). Khan suggests a term of the form Eu for the interfacial resistance to mass transfer:

$$\frac{\frac{F_{liq}}{F_{gas}} \left(\frac{k_1}{k_2} \right)}{\left[1 + \frac{F_{liq}}{F_{gas}} \frac{k_1}{k_2} \right]^2} \cdot \frac{F_{liq}}{k \cdot \sigma} u \quad (8)$$

where σ is the surface area per unit column length. This term may be of importance particularly at high flow-rates and low specific surface areas. Lastly, he suggests a term, F/u , for longitudinal diffusion in the liquid phase,

$$2 \frac{F_{liq}}{F_{gas}} \cdot \frac{k_1}{k_2} \cdot \frac{D_{liq}}{u}$$

This term is presumably very small.

Effect of Temperature and Solute on Plate Height

It is worth examining the qualitative effects of temperature and solute on the terms of the van Deemter equation. This discussion follows, with some extensions, an analysis by Keulemans and Kwantes (36). The effects on the terms suggested by other workers will not be dealt with in detail but some experimental results from the literature will be quoted.

The eddy diffusion term as was stated previously is independent of temperature and of solute. Molecular diffusion in the gas phase involves the diffusivity of the solute in the gas. An empirical equation has been developed by Gilliland (17) for gas diffusivity

$$D_{AB} = \frac{0.0043 T^{3/2}}{P(V_A^{1/3} + V_B^{1/3})^2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}$$

where

D_{AB} is the diffusivity of A in B, $\text{cm}^2/\text{sec.}$,

T is the absolute temperature,

M_A and M_B are the molecular weights of A and B,

P is the total pressure in atmospheres and,

V_A and V_B are the molecular volumes of A and B.

It can be seen that a rise in temperature will increase the gas diffusivity and broaden the plate. An increase in the molecular weight of the solute will not greatly effect the $\left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}$ term when the carrier gas is helium or hydrogen since the molecular weight of the solute will generally be large compared with that of these carrier gases. However, the molecular volume term will be increased with increase in molecular weight in a homologous series which will decrease the diffusivity and decrease the plate height.

The temperature dependence of resistance to mass transfer in the liquid phase is rather complex. Both the distribution coefficient, K' and the diffusivity, D_{liq} are affected. Plots have been made (figure 5) of the distribution coefficient terms K' and $\frac{K'}{(1 + K')^2}$ against temperature. Data for these plots were obtained from the plots of $\log V_g$ against $1/T$ given for ethyl, n-propyl and n-pentyl alcohols by Littlewood et al. (39). The value of $\frac{K'}{(1 + K')^2}$ increases with temperature up to a maximum value where $K' = 1$ and then falls. The temperature corresponding to the maximum is above that which would normally be used and therefore this term may be considered to increase plate heights with increase in temperature. Diffusion in the liquid, to which mass transfer is inversely proportional, increases with increase in temperature. The Einstein equation (11) for diffusion in a liquid state:

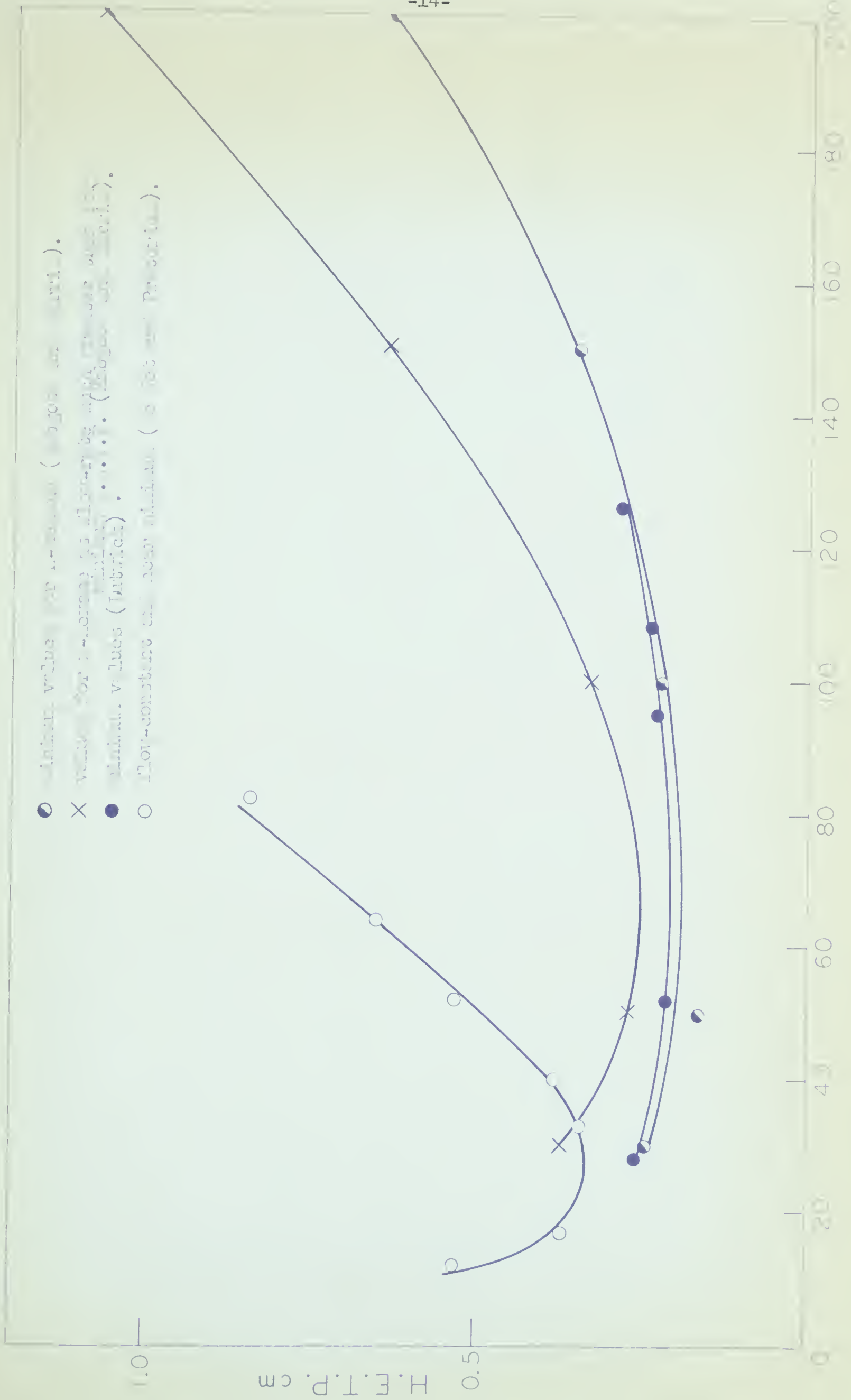
$$D_{\text{liq}} = \frac{kT}{6\eta r}$$

where k is Boltzman's constant, η is the viscosity of the solvent and r is the radius of the solute molecule (assumed spherical). Since the viscosity of a liquid is decreased with increase in temperature, the diffusion coefficient is increased all the more strongly. The plate height due to this factor is thus decreased by a rise in temperature. Since the two factors in the mass transfer term oppose one another it can be seen that the mass transfer contribution may increase or decrease with temperature depending on the relative contributions of the two factors.

Some experimental effects of temperature on plate height are shown in Figure 3. These are measurements by de Wet and Pretorius (7) of H.E.T.P. at a constant velocity near the minimum for n-pentane as solute on a column of liquid paraffin on Celite, and measurements of H.E.T.P. vs. temperature data at high velocities where C is the major contributor to H obtained by Habgood and Harris (27) and by Lutwick (40). Qualitatively, the curves are of the same general shape. They all pass through a minimum.

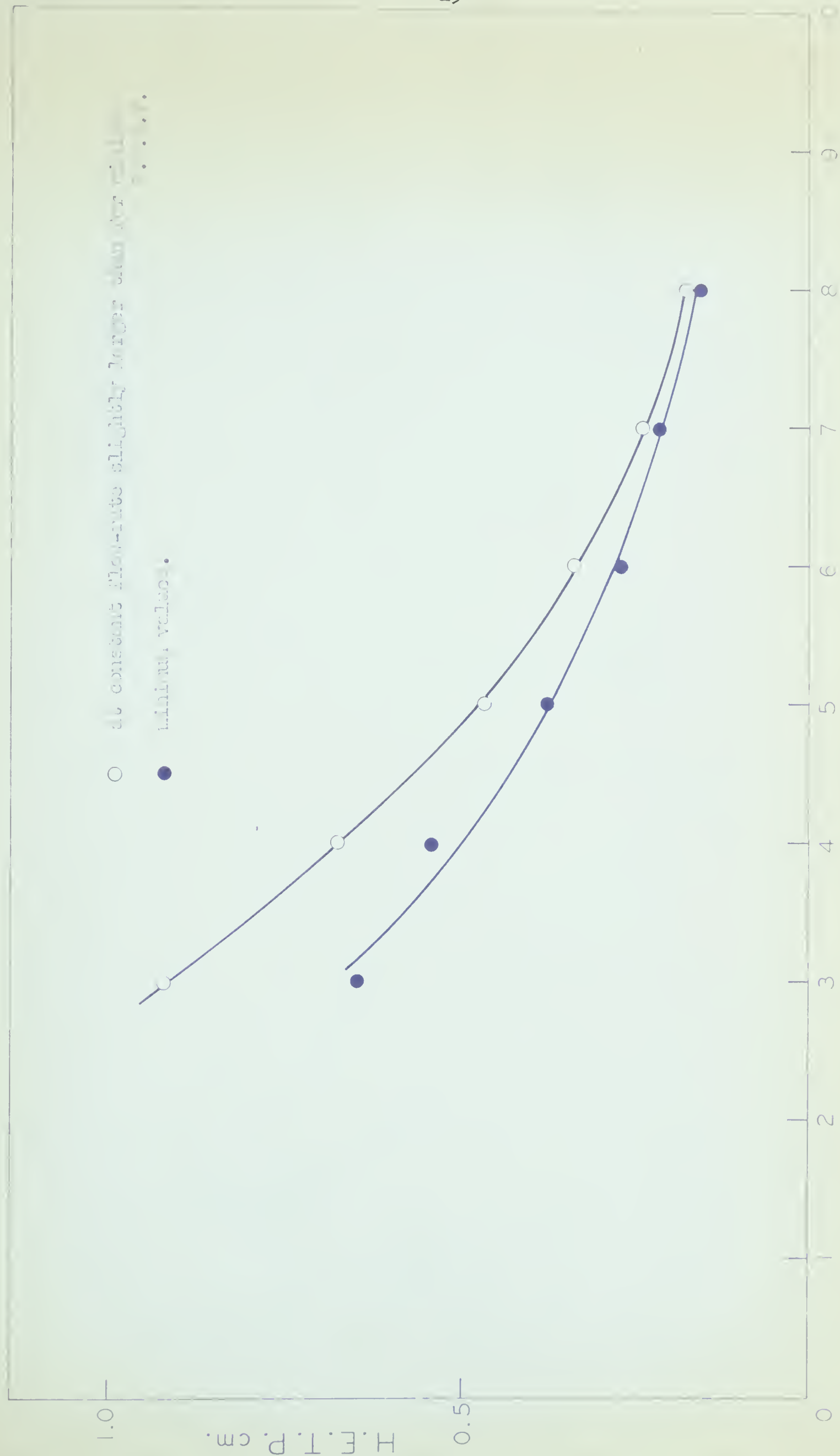
Variation of C from one solute to another at constant temperature will occur because of changes in K' and D_{liq} . As seen in Figure (5), increasing K will decrease term $K'/(1 + K')^2$ for most temperatures. It is difficult to generalize about D_{liq} . In Figure (4) plots of carbon number against H.E.T.P. for two velocities one near the minimum and one above show a decrease for the homologous series propane to n-octane. Data for this plot were obtained from Habgood and Harris (27) and show the dominance of the $K'/(1 + K')^2$ term.

On the other hand Duffield and Rogers (10) found H to decrease with increase in V_R (i.e. increase in K') for three C_6 compounds not in a homologous series.



TEMPERATURE °C

- initial values for a mixture (solid circles).
- × values for a mixture at different flow rates (crosses).
- initial values for a mixture (open circles).
- flow-constant initial values for a mixture (open circles).

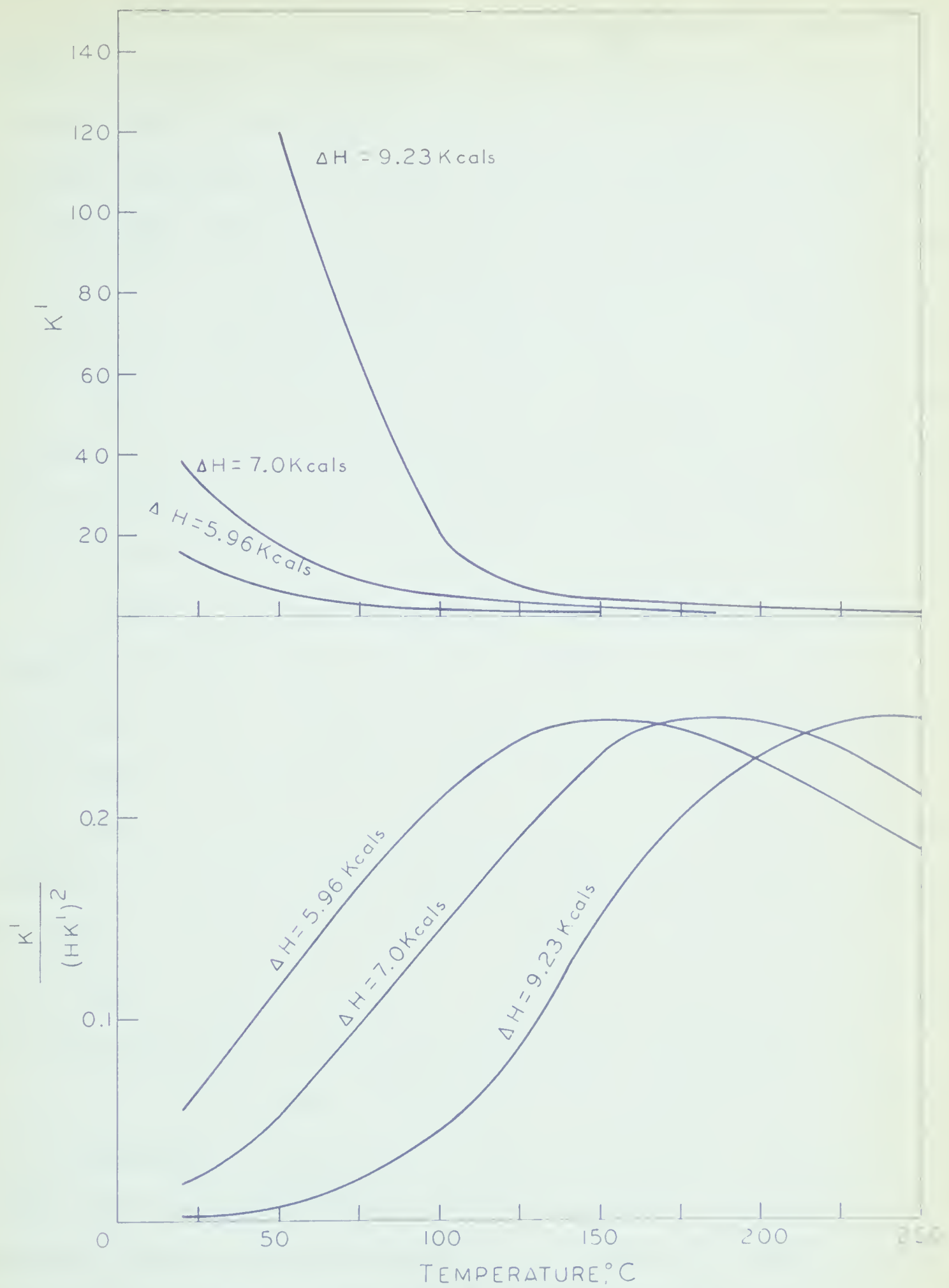


○ at constant flow-rate slightly larger than for minimum velocity.
● minimum velocity.

CARBON NO.

H.E.T.P. cm.

... ..



Plot of $\log K'$, $K'/(1 + K')$, and $K'/(HK')^2$ vs. Temperature.

Fig. 2

B. PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY

The raising of the temperature of a chromatographic column was a logical development from isothermal chromatography. When a mixture of components with a wide range of boiling points is submitted to gas chromatographic separation at a constant temperature closely spaced peaks of the components with lower boiling points are followed by peaks at much greater intervals of the higher boiling compounds. Raising the temperature continuously during the course of the elution lessens the time taken for the higher boiling materials to come through the column and also gives chromatographic peaks which are more uniform in shape. Thus the wide variation in peak height to peak width ratio so often seen in isothermal chromatograms is largely prevented and quantitative measurements are made easier.

A number of workers have made use of the technique of programmed temperature chromatography, in which the temperature of the column is continuously raised. To insure attaining reproducibility of the temperature program two procedures have been followed. The first way is to supply heat to the column at a uniform rate (e.g. by supplying a constant voltage to a resistance heater) and prevent heat loss as much as possible. This gives a gradually falling rate of temperature rise but if conditions are exactly the same each time, the temperature program will be reproduced. The second method is to maintain a uniform rate of temperature rise.

The following papers have been published on programmed temperature gas chromatography. Green and co-workers (21 - 23) have used columns of alumina and of activated charcoal continuously heated during elution to separate mixtures of low-boiling gases and hydrocarbons. Griffiths and his colleagues (24) used partition columns which were heated during the elution to separate mixtures of alkyl chlorides. Willard et al. (13, 20)

used a partition column to separate organic bromides. Drew and McNesby (9) separated air and hydrocarbons on columns of Vycor glass and Pelletex. Guild and his fellow-workers (25) separated mixtures of hydrocarbons, particularly motor gasoline. Ryce and Bryce (45) used partition columns to separate volatile organic sulfur compounds and pentanes. McFadden (42) used partition columns raised in temperature at a constant rate to separate alkyl halides. Dal Nogare and co-workers (3, 4) described an apparatus for maintaining a uniform rate of temperature rise. They separated mixtures of hydrocarbons and of alcohols. Harrison and his colleagues (29) also describe a device for raising the temperature of a column, linearly, reproducibly, and at a controlled rate. Sullivan and his co-workers (47) describe the nonlinear programmed temperature chromatographic separation of some mercaptans and organic sulfides. Eggertsen and his colleagues (12) used programmed temperature chromatography on hydrocarbon mixtures to obtain information analogous to that obtained from analytical distillations.

Theory of Programmed Temperature Chromatography

The relation between isothermal retention volumes and linear program temperature retention volumes has been determined by Habgood and Harris (26). Their development will be reproduced here as a foundation for further development in the theory of programmed temperature chromatography.

Let F = flow rate measured at 25°C and corrected to a mean column pressure.

V_T = retention volume at constant temperature, T , measured from the time of injection, $t = 0$ to $t = t_R$ where t_R = retention time, i.e. time from injection of the sample to emergence of the maximum concentration of the solute
 r = rate of temperature rise of the column.

The retention volume at constant temperature is the integrated total carrier gas flow from the time of injection of the sample until the emergence of the maximum concentration of solute.

$$V_T = \int_0^{t_r} \bar{F} dt \quad (9)$$

Since V_T is a constant for a particular component, equation (9) may be changed to

$$\int_0^{t_r} \frac{\bar{F}}{V_T} dt = 1 \quad (10)$$

but

$$dt = \frac{dT}{r}$$

since the temperature is rising at the rate of r degrees per minute.

If T_0 is the temperature of the column at the time of injection, t_0 , and T_R is the temperature at the time of emergence, t_R , of the peak maximum, then equation (10) may be written as

$$\int_{T_0}^{T_R} \frac{\bar{F}}{r} \frac{1}{V_T} dT = 1 \quad (11)$$

If the ratio \bar{F}/r is kept constant it may be taken outside the integral to give

$$\int_{T_0}^{T_R} \frac{dT}{V_T} = r/\bar{F} \quad (12)$$

For any particular column and solute the retention temperature, T_R , from a given initial temperature, T_0 , will depend only on the ratio r/\bar{F} . The relationship may be determined from isothermal retention volumes by making the indicated integration or determined directly by a number of r/\bar{F} programs. Curves relating r/\bar{F} to temperature are useful for giving expected retention temperatures for various programs.

For the evaluation of the integral in equation (12) advantage may be taken of the linear dependence of $\log (V_T - V_{d.s.})$ on the reciprocal temperature. From plots of $\log (V_T - V_{d.s.})$ against reciprocal temperature, values of retention volume can be obtained which on adding $V_{d.s.}$ for the particular apparatus will give V_T . If plots of $1/V_T$ against temperature are made, then the required integrals are the areas under the curves from the arbitrary starting temperature to higher temperatures.

The effect of gradients in pressure and velocity along the column were neglected since it was felt that the ratio of the velocity of the solute relative to that of the carrier gas was increased so strongly with rising temperature towards the outlet that the pressure effect would be negligible except for columns in which the ratio of inlet to outlet pressure is very high.

Dal Nogare and Langlois (5) have derived an expression for the retention time in a programmed temperature chromatogram which takes account of the change in pressure along the column. Their expression with a change in nomenclature to conform with symbols used so far is:

$$t_r = \int_0^L \frac{\sqrt{1 + (2JMT/P_0^2) (1 - \frac{x}{L})} P_0 M_g A (1 + a \exp b/T)}{MRT} dx \quad (13)$$

where

p_i and p_o are the inlet and outlet pressures, respectively, (to the column), x is the distance from the column inlet, L is the column length, R is the gas constant, M is the mass flow rate of carrier gas in grams per minute, M_g is the molecular weight of carrier gas, A is the cross-sectional area of mobile phase, a and b are constants, r is the rate of temperature rise of column, and J is a temperature dependent

parameter proportional to the viscosity of the carrier gas and the resistance to flow afforded by the packing.

The form of this equation is similar to that of Habgood and Harris in that it involves a term connected to the dead-space of the column and a term related to the distribution coefficient of the solute.

Resolution of Components

A number of definitions of resolution or separating efficiency in gas chromatography have been proposed. The resolving power of a solvent for a particular pair has been defined by Ober (43) as the time interval between the peak maxima of a pair of solutes divided by the average elution time.

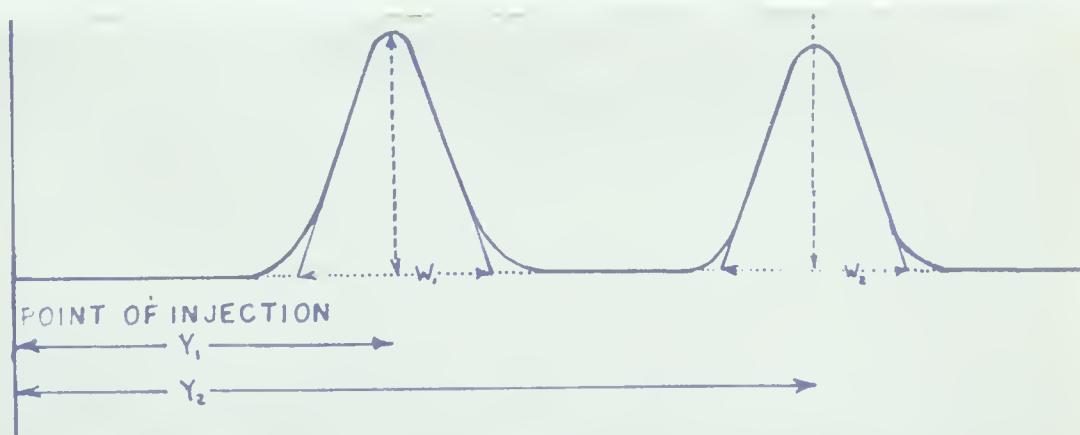


Fig. 6

From Figure 6 where Y = retention time,

$$\text{Resolving Power} = \frac{Y_2 - Y_1}{1/2(Y_2 + Y_1)} \quad (14)$$

Jones and Kieselbach (33) have proposed the same quantity but with only Y_2 in the denominator rather than the average. While Ober's expression is preferable, it is incomplete since it takes no account of peak width. It is, in fact, equivalent to what is designated as intrinsic resolution later in this thesis.

Resolution has been defined by the Nomenclature Committee of the second Symposium on Gas Chromatography at Amsterdam (14) as the difference in retention volumes divided by the average peak widths. If V_A and V_B are the respective retention volumes, then

$$\text{Resolution} = \frac{V_B - V_A}{1/2(W_1 + W_2)} \quad (15)$$

This is the definition used in the present work.

Glueckauf (18) has treated the subject in terms of fractional band impurity.

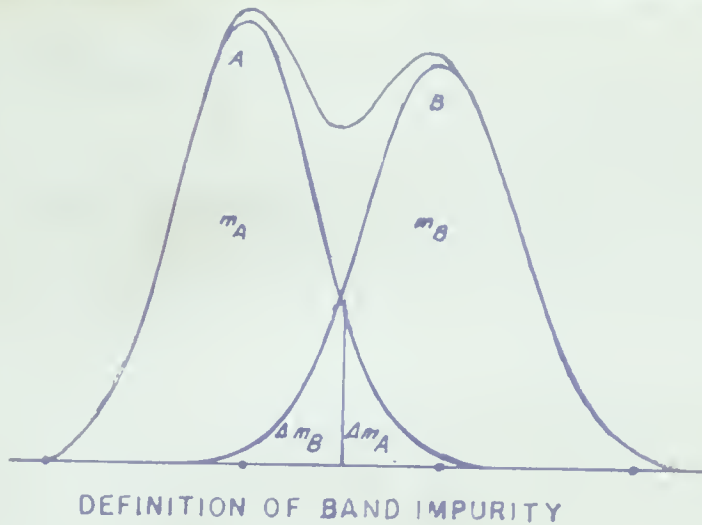


Figure 7 shows the overlapping bands for components A and B with m_A moles of A and m_B moles of B respectively. The portion of B which is present in A is represented by Δm_B and the portion of A present in B is represented by Δm_A .

If the cut is made so that the fractional band impurities are equal

$$\eta_A = \frac{\Delta m_B}{m_A - \Delta m_A} = \eta_B = \frac{\Delta m_A}{m_B - \Delta m_B} \quad (16)$$

where η_A and η_B are the respective fractional band impurities.

Glueckauf arrives at the equation

$$\eta = \frac{2 m_A m_B}{m_A^2 + m_B^2} \left(0.5 - \int_0^f(N, \alpha) e^{-\frac{1}{2}t^2} dt \right) \quad (17)$$

where $f(N, \alpha) = \sqrt{N} (\alpha^{\frac{1}{4}} - \alpha^{-\frac{1}{4}})$

and α is the ratio of the distribution coefficients of the two components.

A set of curves relating the number of plates N , the separating factor, α , and the fractional band impurity, η , have been constructed. These have

been plotted on logarithmic probability paper on which parallel straight lines for constant values of α' relate the number of plates and the fractional band impurity. This plot has been reproduced by Keulemans (36).

DEVELOPMENT OF THEORY OF RESOLUTION IN PROGRAMMED TEMPERATURE
GAS CHROMATOGRAPHY

As has been stated earlier the main objective of this work has been to study the factors contributing to resolution in programmed temperature gas chromatography as an aid towards indicating the optimum conditions of operation to achieve a given separation.

While a number of papers have appeared recently dealing with the theory of programmed temperature gas chromatography, none has considered this very important aspect.

The definition of resolution in programmed temperature chromatography which is proposed is the one which is most commonly used in isothermal gas chromatography, namely

$$\text{Resolution} = \frac{V_A - V_B}{\Delta V_{\text{ave}}}$$

where V_B and V_A are the volumes to the first and second peak maxima, respectively and ΔV_{ave} is the average of the volumes corresponding to the peak widths.

The separation $V_A - V_B$ and the peak width ΔV_{ave} will be examined separately.

In programmed temperature gas chromatography the volumes V_A and V_B may be calculated as follows:

$$V_A = \frac{T_A - T_0}{r} \cdot F \quad (18)$$

where T_A is the retention temperature of compound A, T_0 is the starting temperature and r and F have their usual meaning. Similarly,

$$V_B = \frac{T_B - T_0}{r} \cdot F \quad (19)$$

and therefore

$$V_A - V_B = (T_A - T_B) \frac{F}{r} \quad (20)$$

since $\frac{F}{r}$ and T_0 are the same for both compounds.

An expression for ΔV_{ave} may be derived from the definition of N:

$$N = \frac{16 (V_{TR})^2}{(\Delta V)^2} \quad (21)$$

therefore

$$\Delta V = \frac{4}{\sqrt{N}} V_{TR} \quad (22)$$

$$\Delta V_{ave} = \frac{4}{\sqrt{N}} V_{TRave} \quad (23)$$

Hereinafter, V_{TRave} will be designated as V_{TR} . Combining equations 20 and 23

$$\text{Resolution} = \frac{V_A - V_B}{\Delta V_{ave}} = \frac{F}{r} \frac{(T_A - T_B)}{V_{TR}} \frac{\sqrt{N}}{4} \quad (24)$$

The expression for resolution may be divided into two parts, one related to the number of theoretical plates $(\frac{\sqrt{N}}{4})$ and the other, $(\frac{F}{r} \frac{(T_A - T_B)}{V_{TR}})$, to the program.

The part of resolution related to program for which the name intrinsic resolution is proposed, will be dealt with in the following work. A number of other workers are presently studying the factors affecting N, and it is felt when a sufficient number of data concerning N from isothermal chromatography are available, more precise correlation can be made with programmed temperature chromatography. Therefore, the principal objective will be to examine this intrinsic resolution:

$$R_i = \frac{F}{r} \frac{(T_A - T_B)}{V_{TR}} \quad (25)$$

The expression for resolution in isothermal chromatography may be developed in an analogous form. Starting from the definition

$$R_T = \frac{(V_A - V_B)}{(\Delta V_{av})_T} \quad (26)$$

one may substitute for the average peak width in terms of the number of plates using the definition for N

$$\sqrt{N} = 4 \frac{V}{\Delta V}$$

Therefore, $\Delta V_{av} = \frac{(V_A + V_B)}{2} \cdot \frac{4}{\sqrt{N}}$ and making the substitution, one obtains

$$R_T = \frac{(V_A - V_B)}{1/2(V_A + V_B)_T} \cdot \frac{\sqrt{N}}{4} \quad (27)$$

By analogy, therefore, one may separate the term $\sqrt{N}/4$ and define the intrinsic isothermal resolution as

$$(R_i)_T = \left[\frac{V_A - V_B}{1/2(V_A + V_B)} \right]_T \quad (28)$$

This quantity may be compared with the programmed temperature intrinsic resolution ; the relative total resolution may then differ by differences between the isothermal \sqrt{N} and the effective programmed \sqrt{N} due to changes of N with temperature. It will be noted that the isothermal intrinsic resolution is limited to a maximum absolute value of 2 (where V_A is infinitely large or negligibly small compared with V_B). There is no such limitation on intrinsic resolution in programmed temperature gas chromatography. Thus programmed temperature gas chromatography offers promise of greater resolution than can be obtained isothermally. This is a major advantage of programmed temperature gas chromatography not previously recognized.

In the limit of high F and low r , programmed temperature gas

chromatography approaches isothermal gas chromatography at the starting temperature and the limiting R_i is the isothermal $(R_i)_T = T_0$.

In the limit of high r and low F , F/r approaches zero and hence, R_i approaches zero.

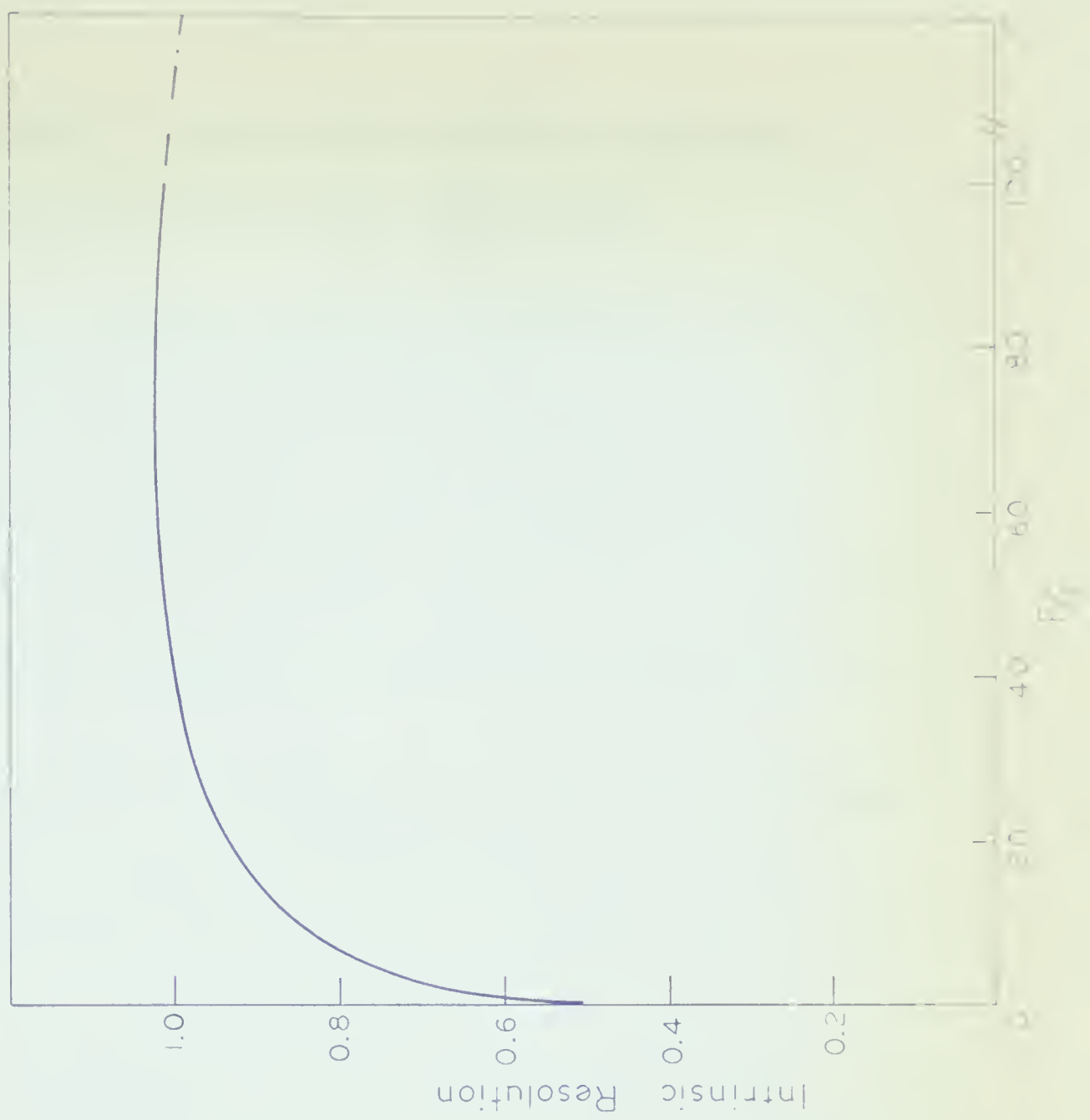
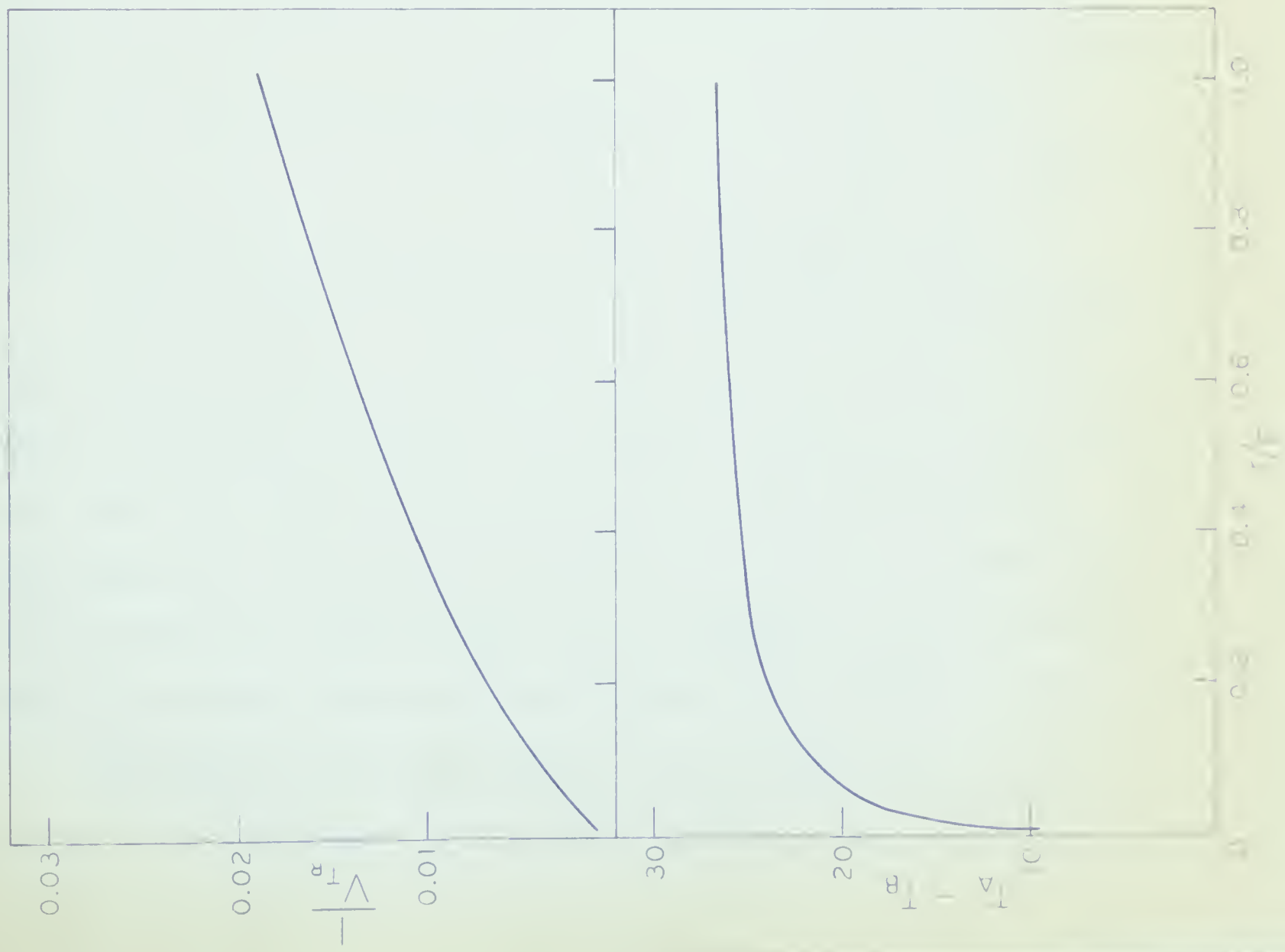
Since the quantities $(T_A - T_B)$ and $1/V_{TR}$ from the theory of programmed temperature gas chromatography are functions of the program defined by ratio of r to F , R_i will be presented in terms of the ratio F/r which is one of its contributing factors. Dal Nogare (5) has presented some isolated observations of resolution in terms of this ratio, F/r .

Although both the terms $(T_A - T_B)$ and $1/V_{TR}$ depend on F/r , their dependence is complex and it was not possible to develop a completely theoretical relationship between R_i and F/r . Therefore, an attempt was made to determine the general relationship from examination of a number of carefully selected situations.

A typical plot of R_i versus F/r is shown in Figure (8) for the pair of compounds n-heptane and n-hexane on a column of Apiezon L. Data were obtained from Habgood and Harris (26). The intrinsic resolution increases rapidly with increasing F/r up to a value of F/r of approximately 20 and then remains fairly constant. The maximum value of the intrinsic resolution reached is in this case very close to the value at $F/r = \infty$ which is the isothermal intrinsic resolution at the starting temperature (30°C). An examination of intrinsic resolution has been made for a number of other compounds.

Fig. 9

variation of resolution as a function of the ratio $\Delta T_R / T_R$ - helium as a function of pressure from a starting temperature of 373°.



APPLICATION OF THEORY TO CALCULATION OF INTRINSIC RESOLUTION
IN PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY

An examination of intrinsic resolution in programmed temperature gas chromatography along with the factors which make up intrinsic resolution has been made. In order that the study may cover any solute-solvent pair that might be found in a practical analysis a number of pairs of hypothetical compounds were chosen varying over a wide range of retention characteristics. Following this some actual compounds were considered.

Retention temperatures were calculated by a numerical integration of equation (12) over intervals from a temperature of 0°K. to higher temperatures assuming linear log V --reciprocal temperature relationship throughout the whole temperature range. Actually, some curvature does occur but for moderate temperature ranges, linearity may be assumed. For the retention temperatures from higher starting temperatures the appropriate section was picked from the plots of retention temperature against r/F . The factors which make up intrinsic resolution, $T_A - T_B$, and $1/V_{T_R}$ were determined and the intrinsic resolution computed. A comparison with intrinsic resolution at constant temperature was made.

In the evaluation of the integral of dT/V_T for the calculation of retention temperature, considerable simplification is possible in the numerical procedure if the dead-space volume is neglected and the retention volume from the air peak is used for V_T . The conditions under which dead-space may safely be neglected are discussed in Appendix III. In the calculations reported here, $V_{d.s.}$ is included in V_T in all cases where the resultant resolution would be affected by more than 1 or 2%.

The intrinsic resolution depends on the solvent, solute, and program but is independent of the actual packing of the column as

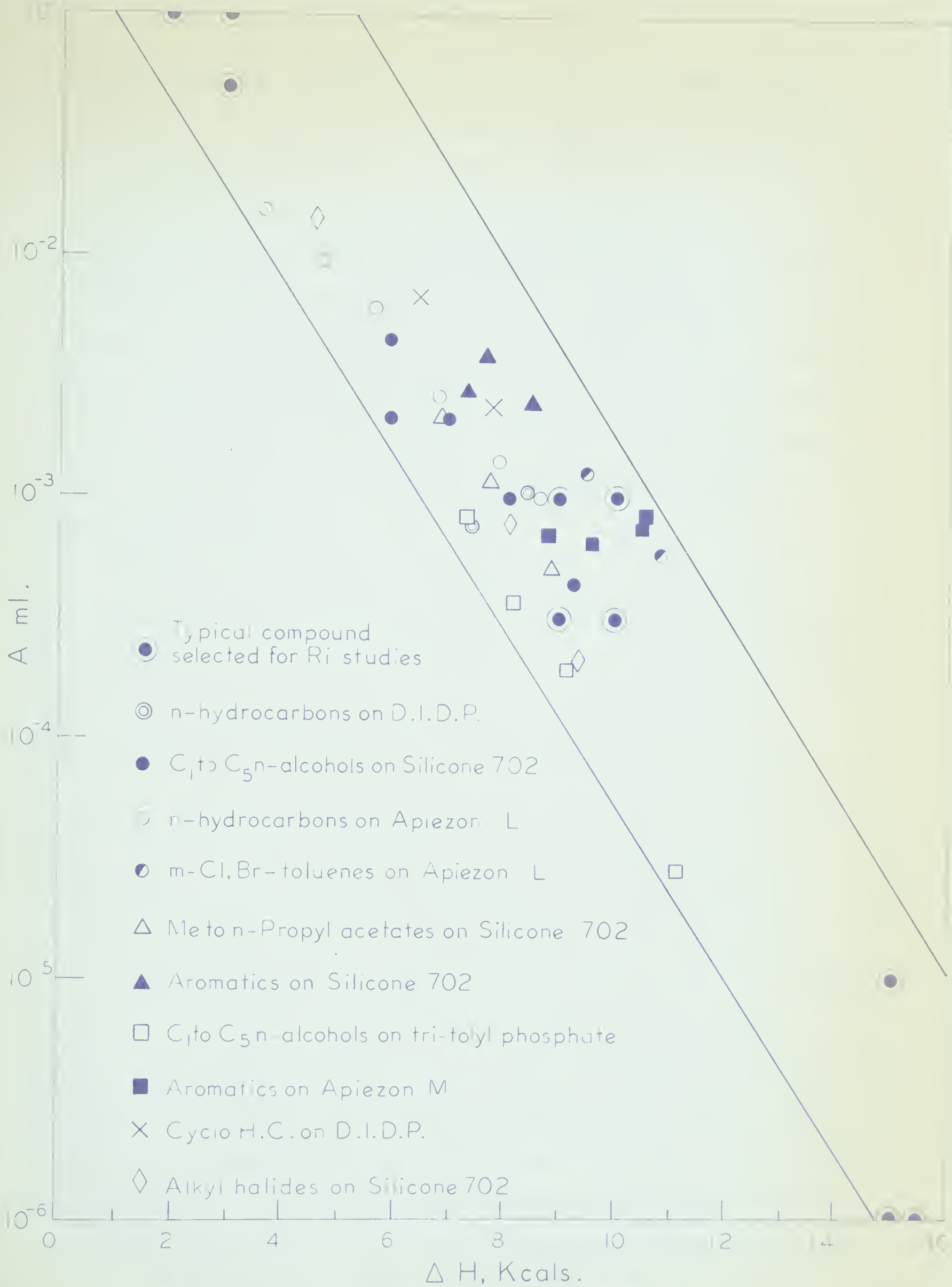
characterized by N. For purposes of practical analysis it is necessary to consider the total resolution which includes the effect of N. While it was considered outside the scope of the present work to attempt a full treatment of the variation of N with temperature and solute —a subject of considerable complication and uncertainty at present —some qualitative conclusions will be stated later. Some examples of actual programmed temperature chromatograms will also be examined.

Choice of Typical Compounds: Heat of Solution, ΔH , and Pre-exponential Factor, A.

In order that resolution could be examined for all likely pairs of compounds that might be encountered in practical analyses, isothermal retention volumes for a number of compounds were examined over a range of temperature. As has already been mentioned, retention volumes at constant temperature are related to temperature by the equation:

$$V_T = A \exp. (\Delta H/RT) \quad (29)$$

Thus isothermal retention behaviour can be characterized by two constants, A and ΔH , which may be calculated from the plot of log retention volume against reciprocal temperature. A survey was made of available isothermal data in the literature together with unpublished measurements. Surprisingly few papers give retention data over a wide enough range of temperature to enable A and ΔH to be accurately calculated. However, Littlewood et al. (39) have given some excellent data and these have been extensively drawn upon. Specific retention volumes, V_g , defined by Littlewood as the retention volumes on a column containing one gram of stationary phase, were used throughout the calculations. The survey included alcohols, acetates and aromatics on columns of Silicone 702 and tritolyl phosphate by Littlewood et al., normal hydrocarbons and halo-

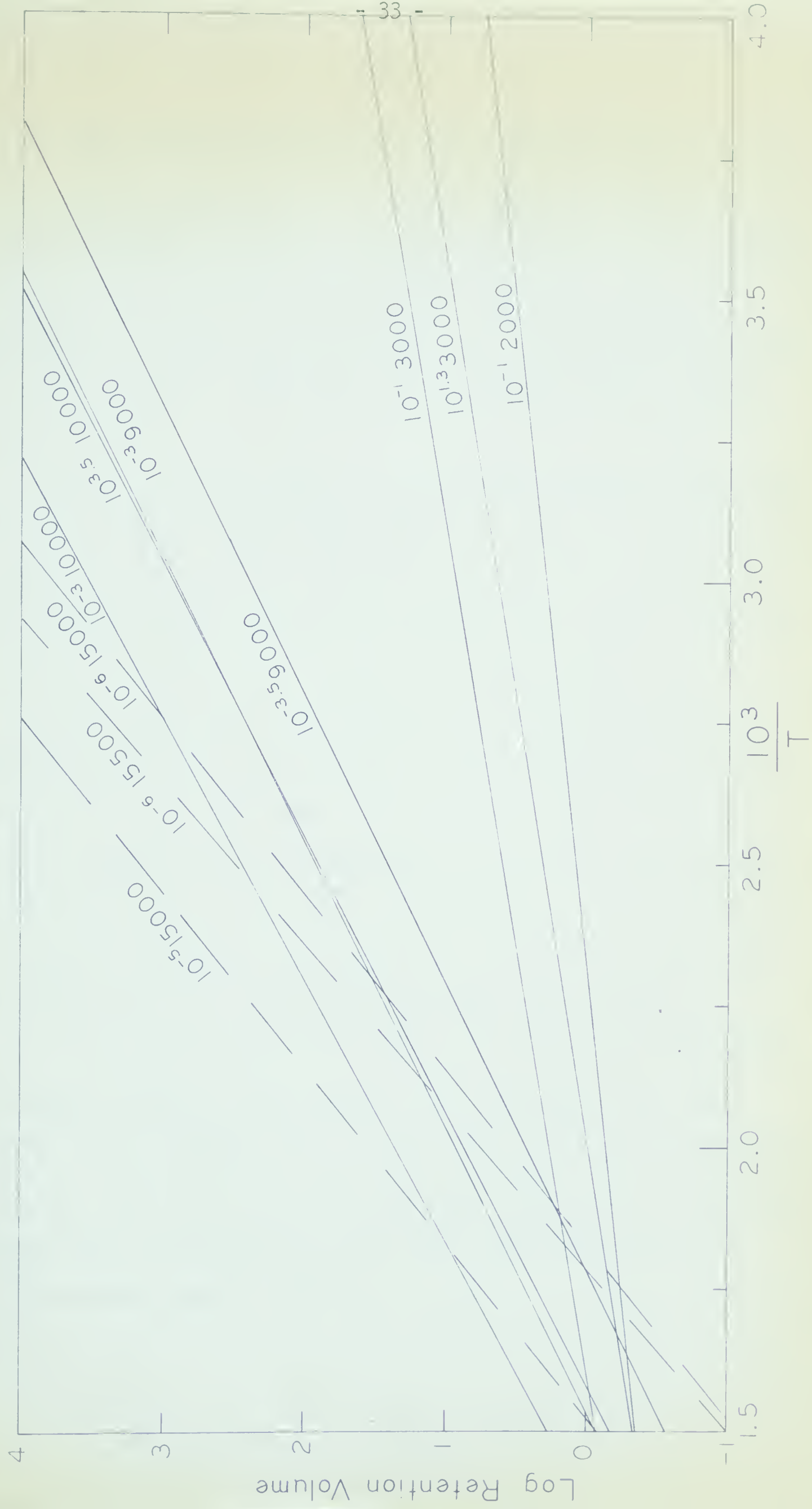


Relation of pre-exponential factor, A , to heat of activation, ΔH .

generated aromatics on a column of Apiezon L by Habgood and Harris (26), alkyl halides on columns of dinonyl phthalate and silicone 702 by Hardy (28), hydrocarbons and alcohols on columns of di-isodecyl phthalate and squalane by Porter, Deal, and Stross (44), and aromatics on a column of Apiezon M which had previously been measured by the author. In figure 9 are shown the plots of A against ΔH on semi-logarithmic paper. It is seen that for each homologous series (sometimes excluding the first member) a linear relationship between $\log A$ and ΔH exists. These various lines were approximately parallel and fell in a band. While only a limited number of series are included they cover a wide range of solvent-solute interaction.

It seems surprising that no previous mention has been made in gas chromatographic papers to this linear relationship of $\log A$ to ΔH . It is perhaps not too unexpected since one of the factors of $\log A$ is an entropy term. One might expect the entropy to parallel the heat of solution since the solute molecules are held more firmly at a high heat of solution and, therefore, presumably would be in a more ordered arrangement. A somewhat similar correlation has been noted by Cremer (2) in kinetic studies. She has pointed out that in heterogeneous reactions the log of the entropy factor is linearly related to the energy factor.

It can be seen from the $\log A$ -- ΔH plot that only one or two values of A for each value of ΔH are necessary to obtain a representative number of isothermal retention volumes covering most solute-solvent possibilities. The hypothetical compounds selected for this study of resolution in programmed temperature chromatography are marked on the A-- ΔH band in figure 9. They represent solute-solvent pairs in which the heats of solution range from very low, through intermediate values to very high.



In each ΔH range the compounds chosen permitted study of R_i for pairs of solutes related either as adjacent members of a homologous series or as members of different series having similar retention characteristics. In the latter case, comparisons were possible for pairs of solutes having the same ΔH and different A 's; the same A and different ΔH 's; and different ΔH 's and A 's but in opposite sense to members of the same series.

Figure 10 shows the plots of $\log V_g$ versus reciprocal temperature for all the hypothetical compounds used in this study. In the figure and hereinafter in text compounds will be identified by the pre-exponential factor and the heat of solution in the following way: $10^{-3.5}$ 9,000 when $A = 10^{-3.5}$ (3.16×10^{-4}) ml. and $\Delta H = 9,000$ calories per mole.

It is interesting to note that order of isothermal elution of members of a homologous series reverses at high temperature according to these plots of $\log V - 1/T$. Such crossing has not been observed experimentally, perhaps because the temperatures involved are somewhat higher than would normally be used for gas chromatography. Also over considerable ranges of temperature the curvature of the ΔH -reciprocal temperature relationship may be sufficient to prevent this crossing.

In the intermediate ΔH range the pair 10^{-3} 9,000, $10^{-3.5}$ 10,000 while being related as adjacent members of a homologous series had retention volumes somewhat closer together than for an actual homologous series pair. Thus resolution difficulties were accentuated. Among the compounds pairs corresponding to more widely separated members of a homologous series could be selected.

The Intrinsic Resolution of some Typical Pairs of Compounds

Figure 11 shows the plots of r/F versus temperature for all compounds considered over integrals from 0°K. to higher temperatures. The calculation of r/F when a different starting temperature is used may be made by adjusting the r/F corresponding to the desired starting temperature to zero and subtracting from the r/F values for higher temperatures the adjustment so made.

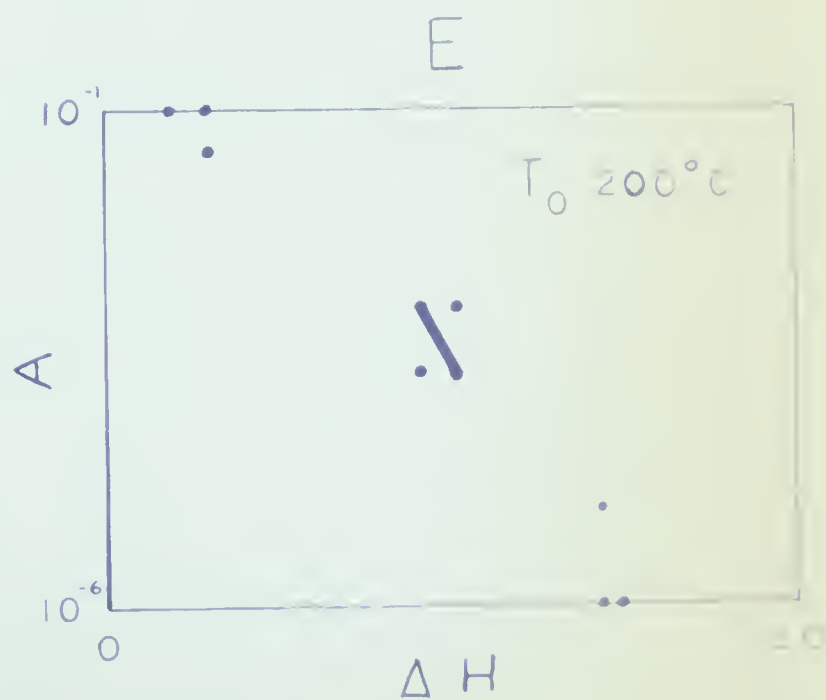
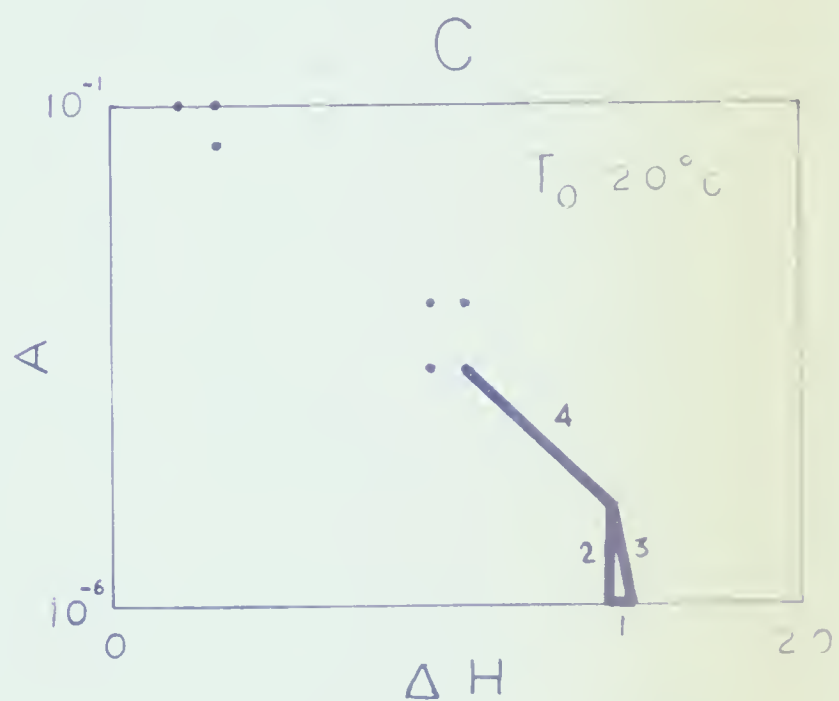
Intrinsic resolution depends on the retention characteristics of the two compounds (ΔH and A) as expressed in the r/F versus T_R plot and on the starting temperature of the programmed temperature chromatograph. It can be seen from Figure 11 that curves of r/F versus T_R tend to all be roughly of the same shape but displaced along the temperature axis according to ΔH . Thus one might expect rather similar behaviour for compounds with low ΔH at low starting temperatures as for compounds of high ΔH at high starting temperatures.

To calculate the intrinsic resolution for a pair of compounds the retention temperatures for various values of r/F are read from the graph. The isothermal retention volumes corresponding to these temperatures can be determined by equation or graph and the respective intrinsic resolutions calculated.

It will be recalled that members of homologous series lie relative to each other in general trend of the band of $\Delta H - A$ values. To illustrate the relation between adjacent members of a homologous series and compounds for different series a number of pairs were chosen from the typical compounds indicated in Figure 9. For various starting temperatures, intrinsic resolution was examined along with the contributing factors $T_A - T_B$ and $1/V_{T_R}$. Plots have been made of $T_A - T_B$ and $1/V_{T_R}$ against r/F and of intrinsic



Fig. 11 Relation of μ to temperature, °C



dependence on character of the
inhibiting substance but the
dependence with low values of α
is similar to a function of α
given with a low value of α in
figure 1.

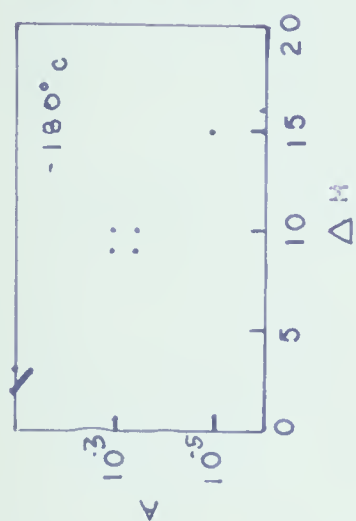
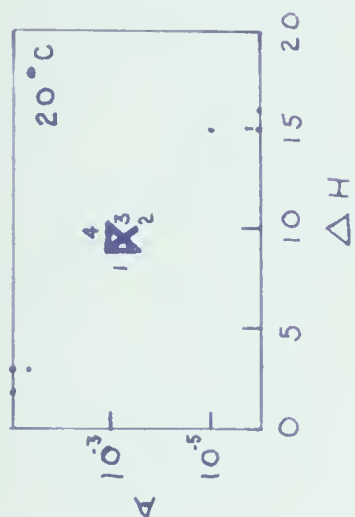
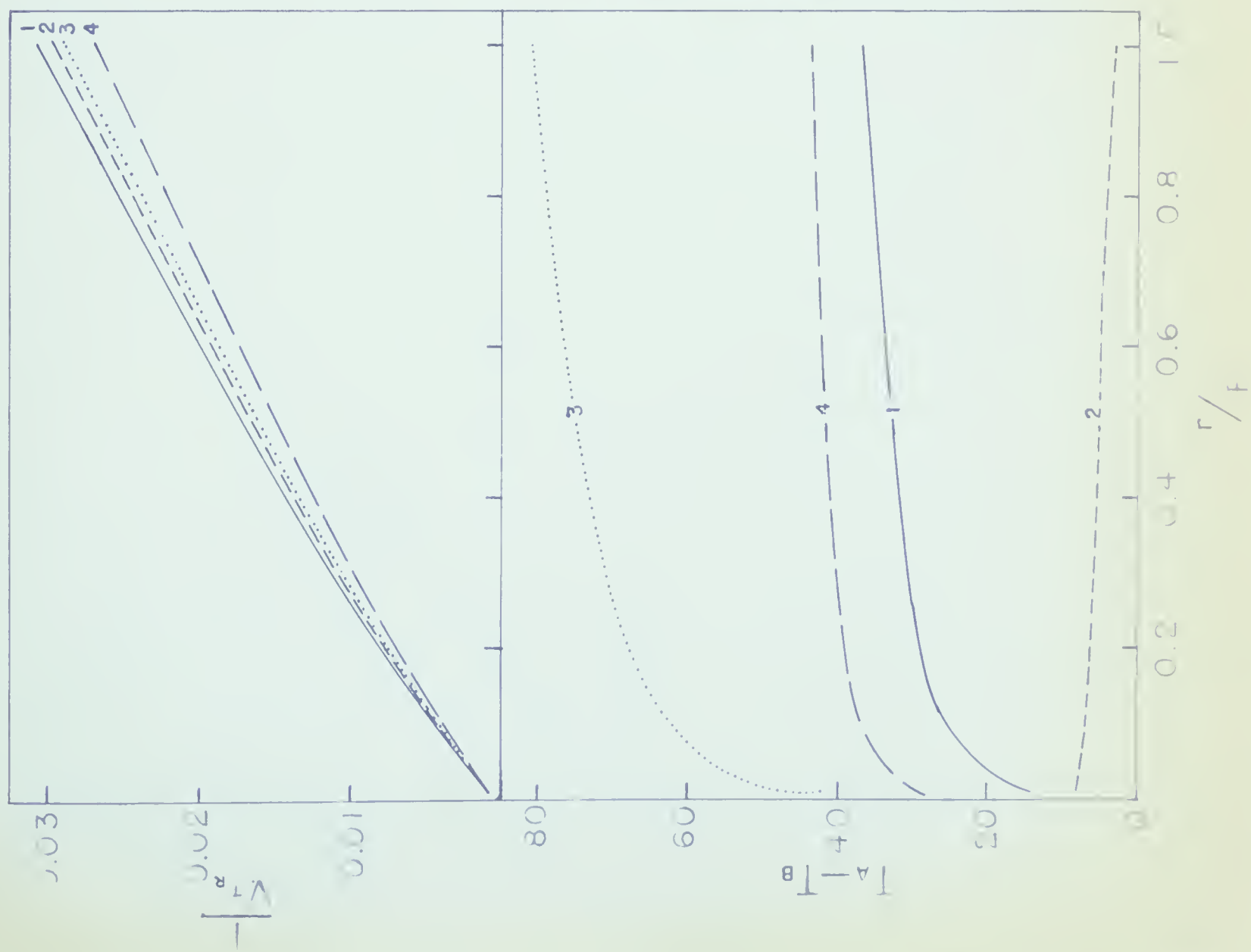


Fig. 14



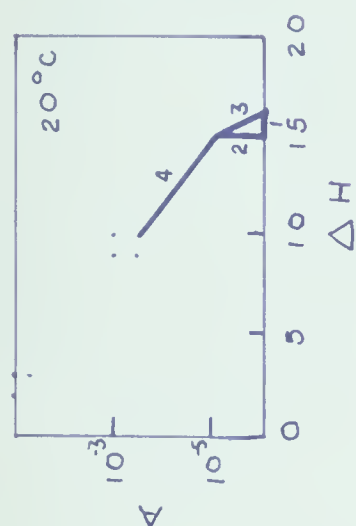
Δ 10 15 20
 ΔH 10³ 10⁴ 10⁵



INTRINSIC VISCOSITY

Fig. 15

Retention characteristics of
intrinsic resolution for series
of substances with different
of solution as a function of
program with a low step in
temperature.



A	$\Delta \bar{I}$	$\Delta \bar{I}$
1. 10^{-6}	15,500	10^{-5}
2. 10^{-5}	15,000	10^{-5}
3. 10^{-5}	15,000	10^{-5}
4. 10^{-5}	15,000	10^{-5}

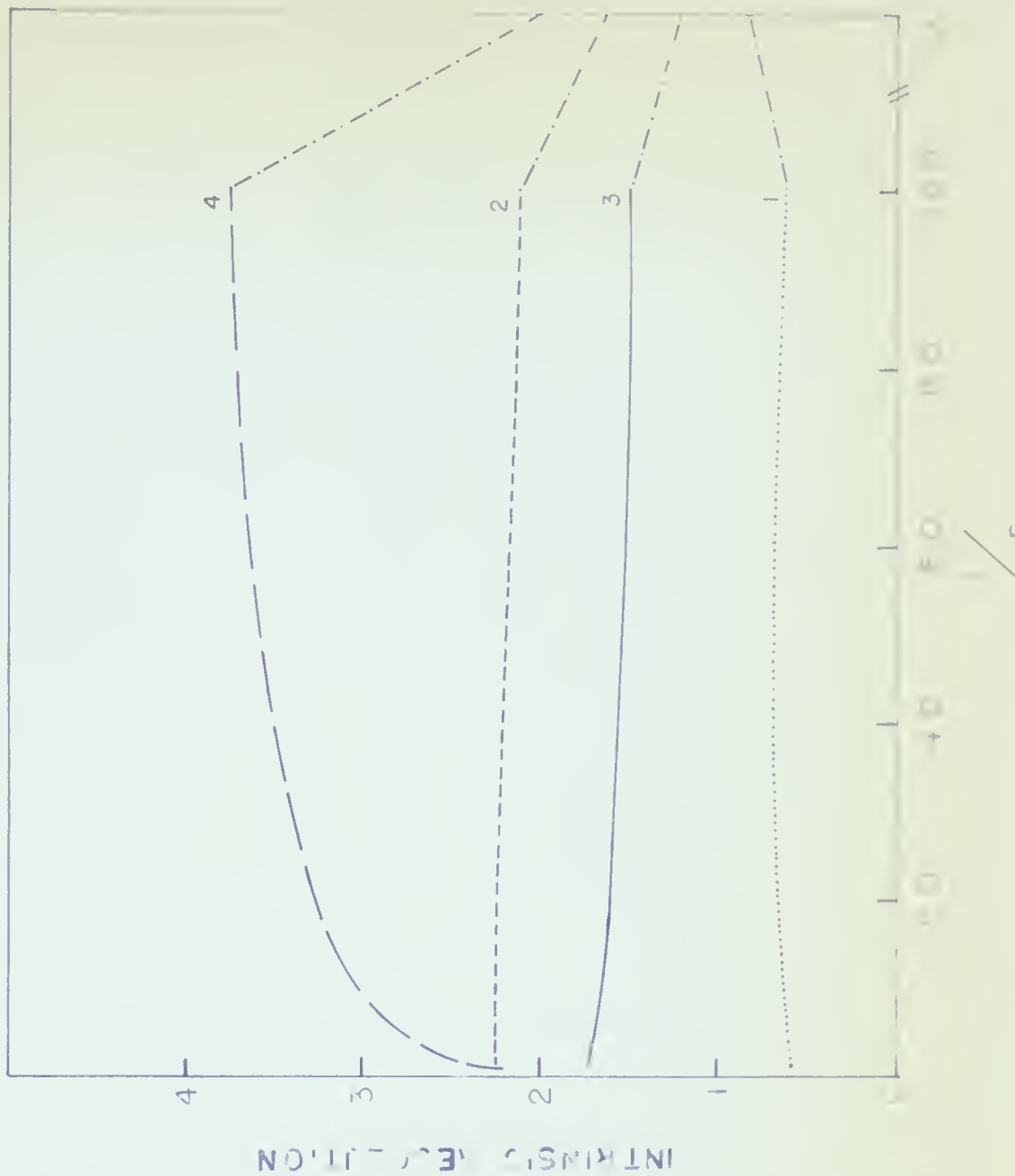
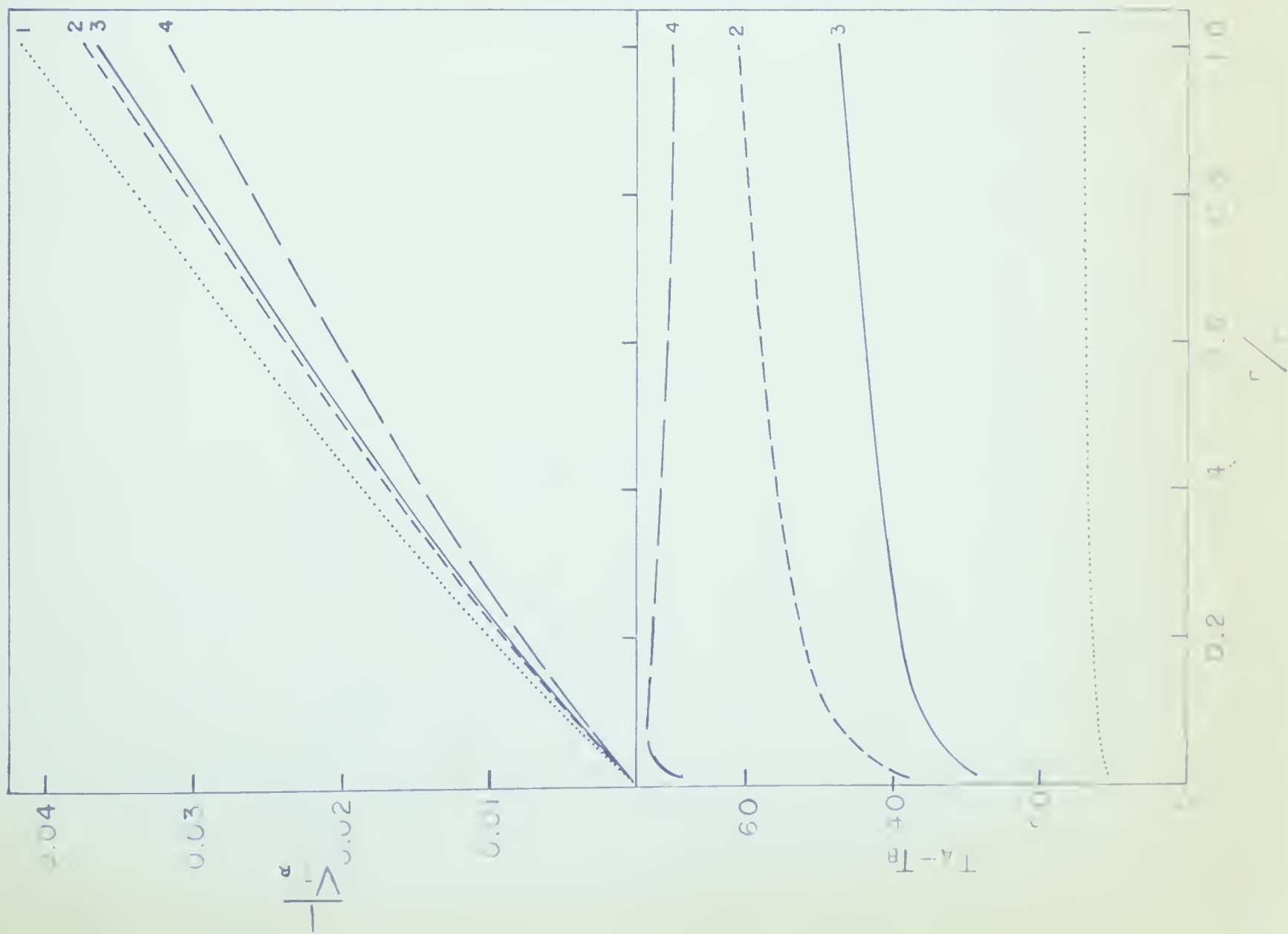
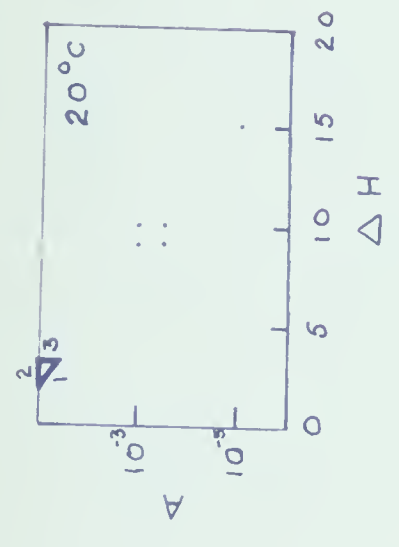
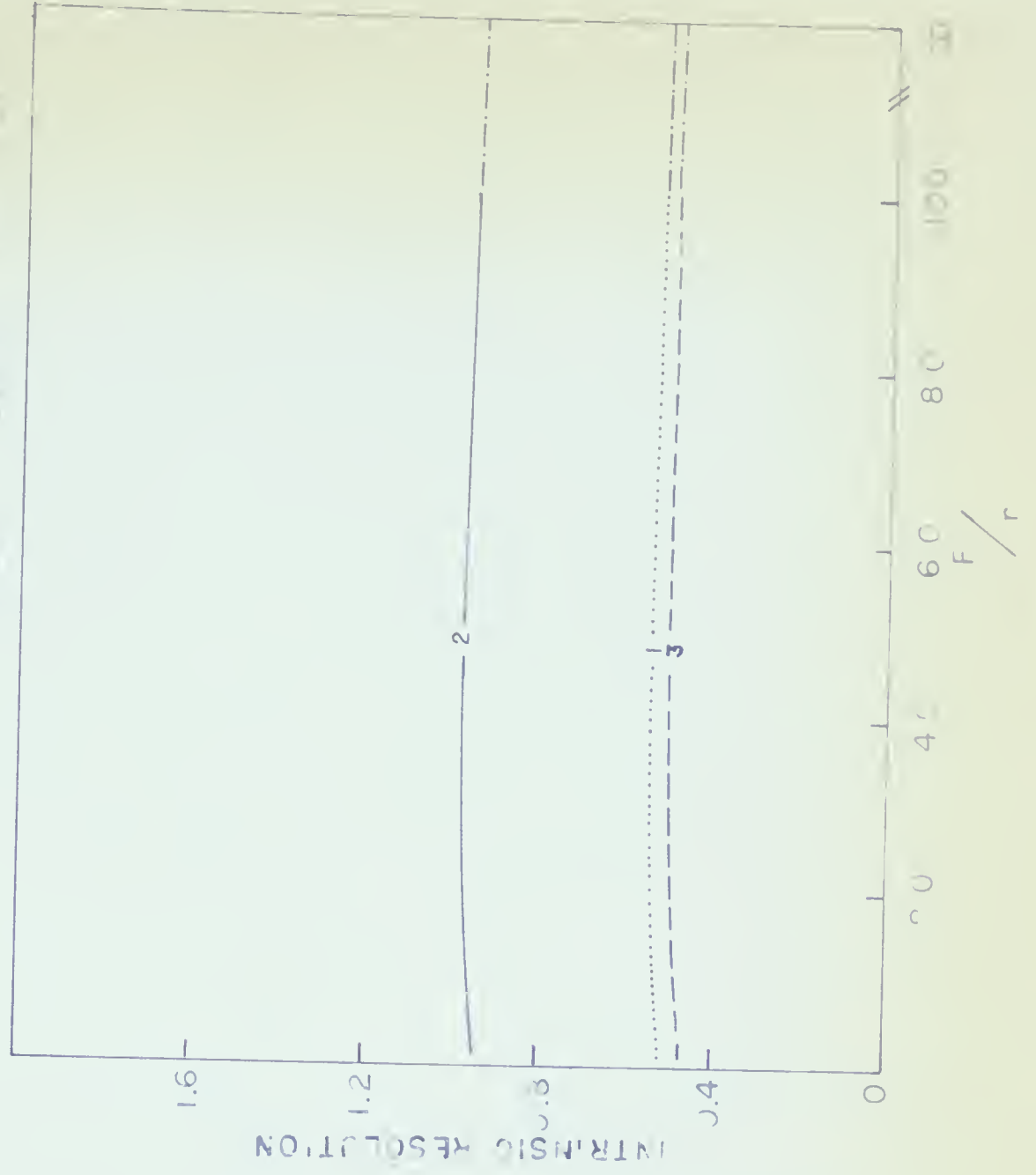
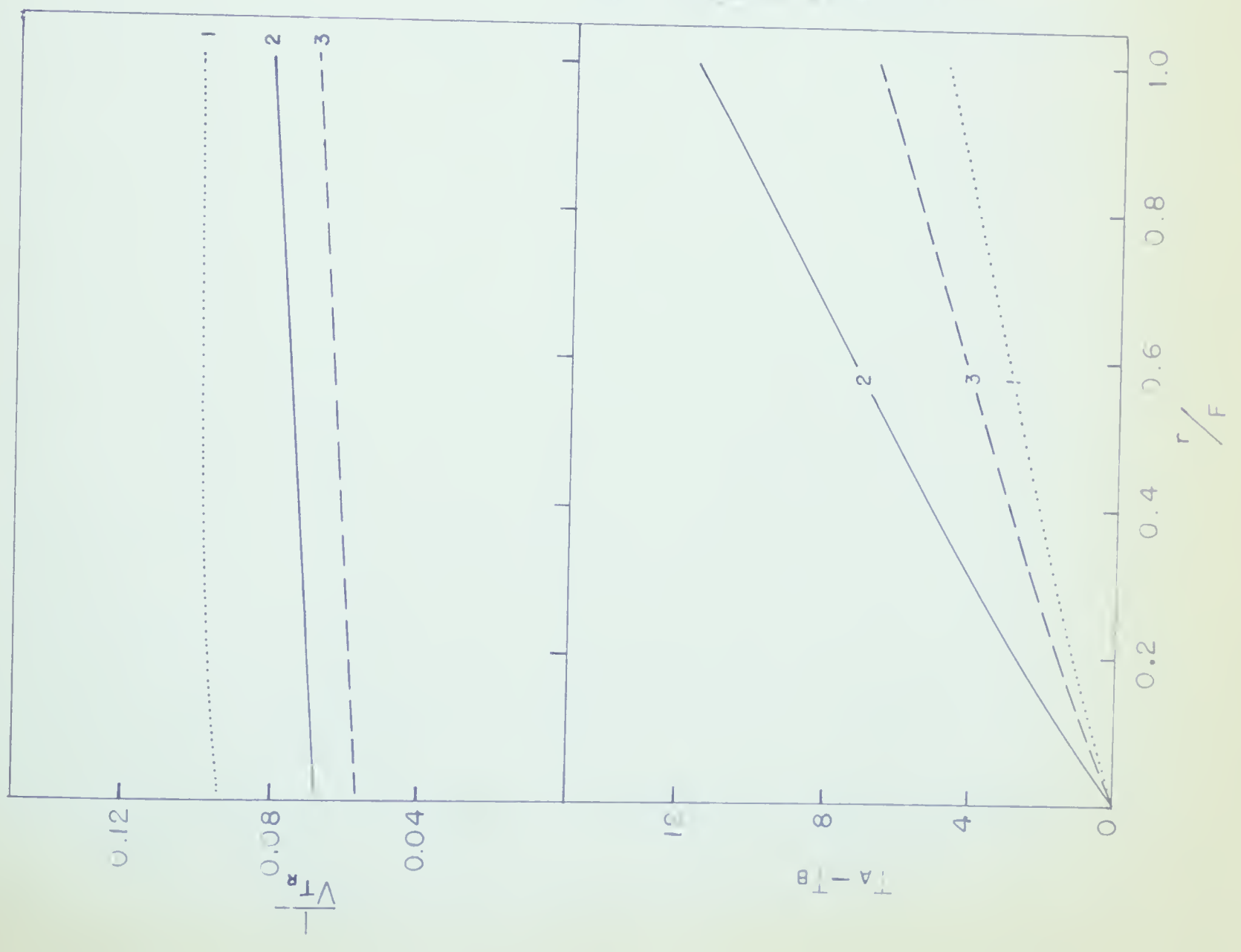


Fig. 1

Retention characteristics of
intrinsic viscosity for
of substances with low
solubility as a function of
gram with a high degree of
structure.



ΔH
1. 1000
2. 100
3. 10



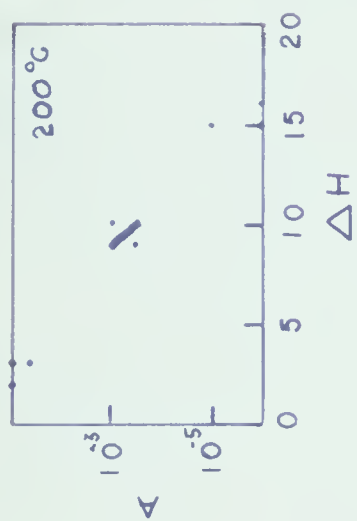
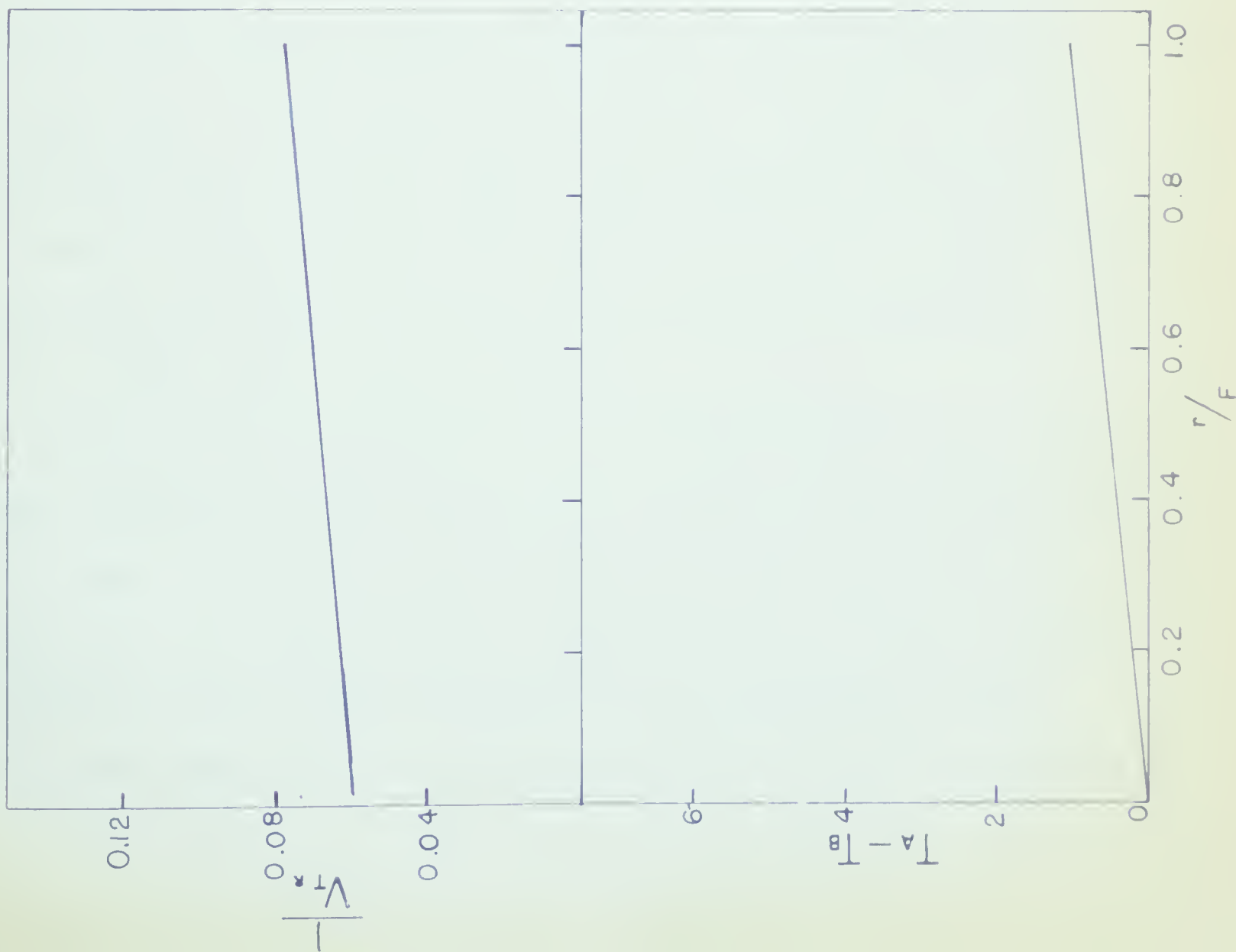
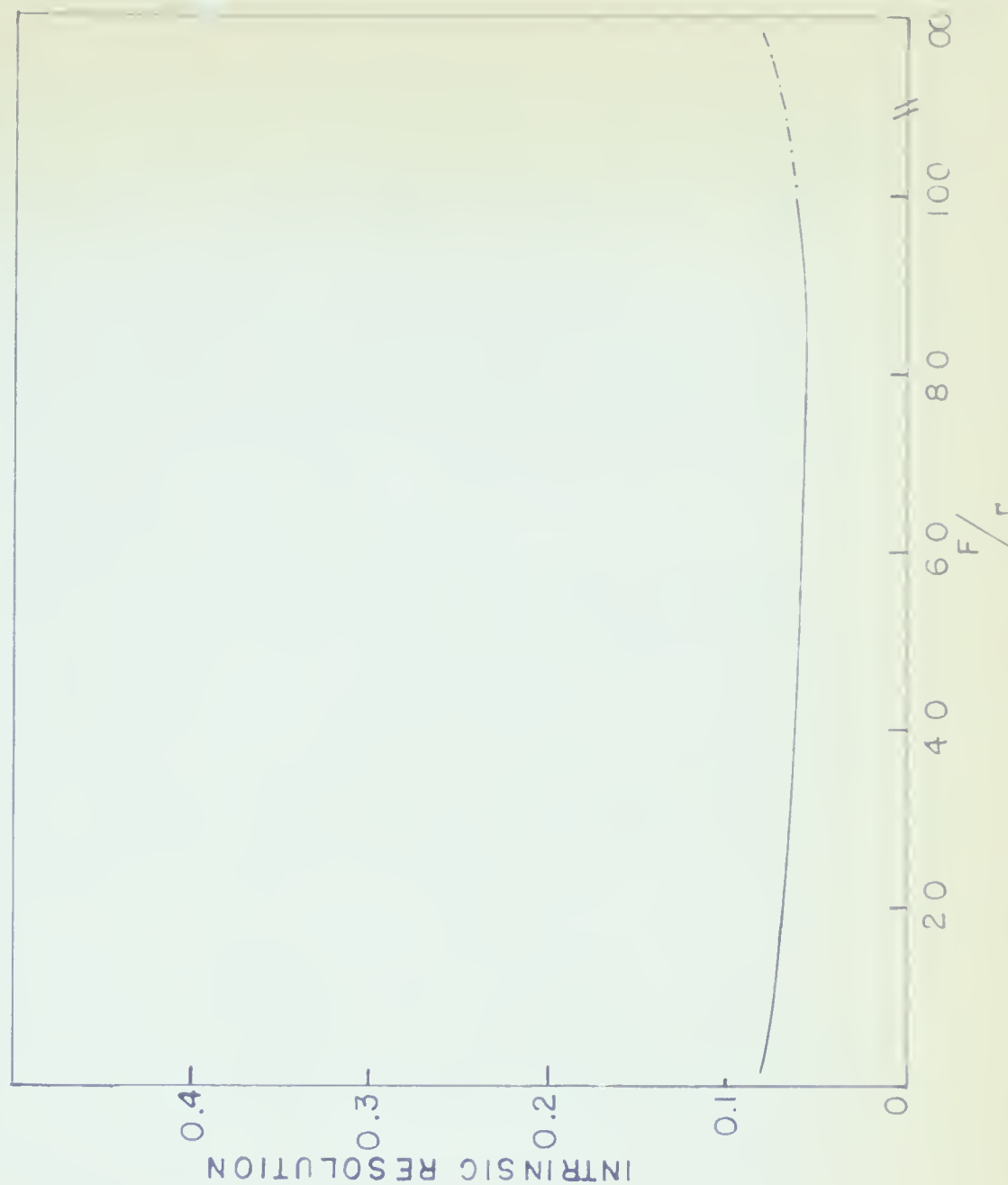


Fig. 17
 A plot of A versus ΔH at 200°C .
 The data points are shown for the
 various temperatures. The
 values of A are in units of 10^{-4} .
 The values of ΔH are in units of 10^3 .

ΔH

ΔH



resolution against F/r . These are shown in Figures 13 to 17 and the various situations considered in these figures are summarized in Figure 12. The compounds are designated in terms of their ΔH and A values as shown in Figure 9 and the pairs for which intrinsic resolution was calculated are joined by heavy lines. Low starting temperatures are illustrated by A, B, and C and high starting temperatures by D and E.

The reciprocal isothermal retention volume term, $1/V_{TR}$, increases with r/F , as seen in each of Figures 13 to 17, since retention temperature increases. As seen in Figures 16 and 17 the rate of increase of $1/V_{TR}$ with temperature falls off with high starting temperature since there is only a small change in retention temperatures for a large change in r/F .

No complete generalization can be made about the term $T_A - T_B$ except that it is zero at $r/F = 0$. For relatively high starting temperature $T_A - T_B$ increases approximately linearly with r/F as seen in Figures 16 and 17.

All curves relating intrinsic resolution to F/r are qualitatively of the same shape. The intrinsic resolution reaches a maximum value which remains approximately constant. There is some variation in the value of F/r at which a steady value is reached but for most pairs of compounds it is reached between F/r 10 and 20. This is seen in Figure 13, Figure 14, Curves 2, 3 and 4, and in Figure 15, Curve 4.

For some pairs of compounds the intrinsic resolution is approximately constant throughout the entire range of F/r examined as shown in Figure 14, Curve 1, Figure 15, Curves 1, 2 and 3, Figure 16, Curves 1, 2 and 3, and in Figure 17. (The limit of intrinsic resolution at $F/r = 0$ must be zero as indicated in theory section heretofore but the relationship was not studied in the region $F/r < 1$) Intrinsic resolution for pairs of compounds

with the same heats of solution but different pre-exponential factors is relatively constant for all values of F/r examined as shown in Figure 14, Curve 1, Figure 15, Curve 2 and Figure 16, Curve 3.

Approximately constant intrinsic resolution is also obtained when programs have been started at relatively high temperatures. Under these conditions $T_A - T_B$ increases approximately linearly with r/F and the $1/V_{TR}$ term is increasing only very slowly with r/F . Therefore, intrinsic resolution remains approximately constant. This is illustrated in Figures 16 and 17. Here it may be noted that, as anticipated, for the compounds with low heats of solution 20°C is a relatively high starting temperature comparable to 200°C for compounds with intermediate or high heats of solution. Further evidence for this is shown in Figure 13 and Figure 15, Curve 4 where for a program starting at a temperature of -180°C . or less, the intrinsic resolution to F/r relationship of a pair of compounds with low heats of solution is similar to the relationship for a pair of compounds with high heats of solution in a program starting at a temperature of 20°C .

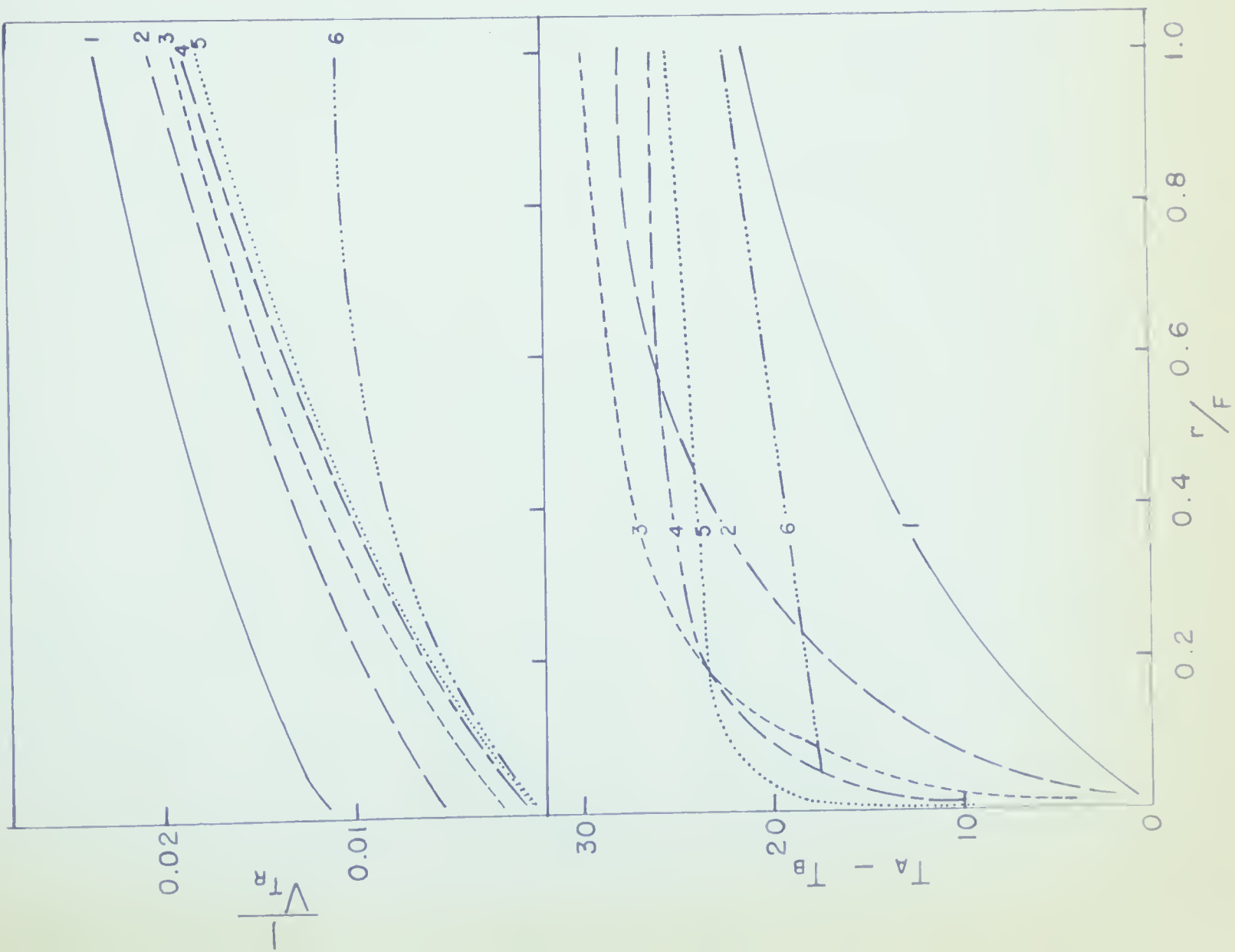
For a given pair of compounds the intrinsic resolution is greater at a lower starting temperature. This is illustrated by Figure 13 and Figure 16, Curve 1 for compounds with low heats of solution and by Figure 14, Curve 2 and Figure 17 for compounds with intermediate heats of solution.

Calculation of Intrinsic Resolution for Two Homologous Series.

To further illustrate the results of the previous section, intrinsic resolution and its component factors were examined for two homologous series using reported isothermal retention volumes. Homologous series were chosen because of the usually greater interest in separation of members of such a series.

Isothermal retention data from the literature for two series were used to calculate programmed temperature gas chromatographic behaviour and intrinsic resolution. The series chosen were the n-alcohols, methyl to pentyl on a column of Silicone 702 as given by Littlewood et al. (39) and the n-hydrocarbons propane to octane along with two aromatic halides (m-Br toluene and m-Cl toluene) on a column of Apiezon L as given by Habgood and Harris (26). In Figure 18 and 19 the retention characteristics and intrinsic resolutions have been plotted for the alcohols and the hydrocarbons respectively. All plots fall into the pattern set in the previous section. It might be noted that the situation in which two compounds have the same heats of solution but different pre-exponential factors is approximately illustrated by methyl and ethyl alcohols on Silicone 702. There, as anticipated, the intrinsic resolution is relatively constant with change in F/r .

The curves of $T_A - T_B$ versus r/F are of interest in that it has been suggested (5) that retention temperature is always a linear function of carbon number (except for, possibly, the first few members of a series). Thus, $(T_A - T_B)$ should be constant for all pairs at any r/F . It can be seen in Figures 18 and 19 that for $r/F = 0.2$ this is approximately true but considerable divergence takes place at other values.



- 1 — $nC_4 - C_3$
- 2 — $nC_5 - nC_4$
- 3 — $nC_6 - nC_5$
- 4 — $nC_7 - nC_6$
- 5 — $nC_8 - nC_7$
- 6 — $m\text{-Br.toluene}$

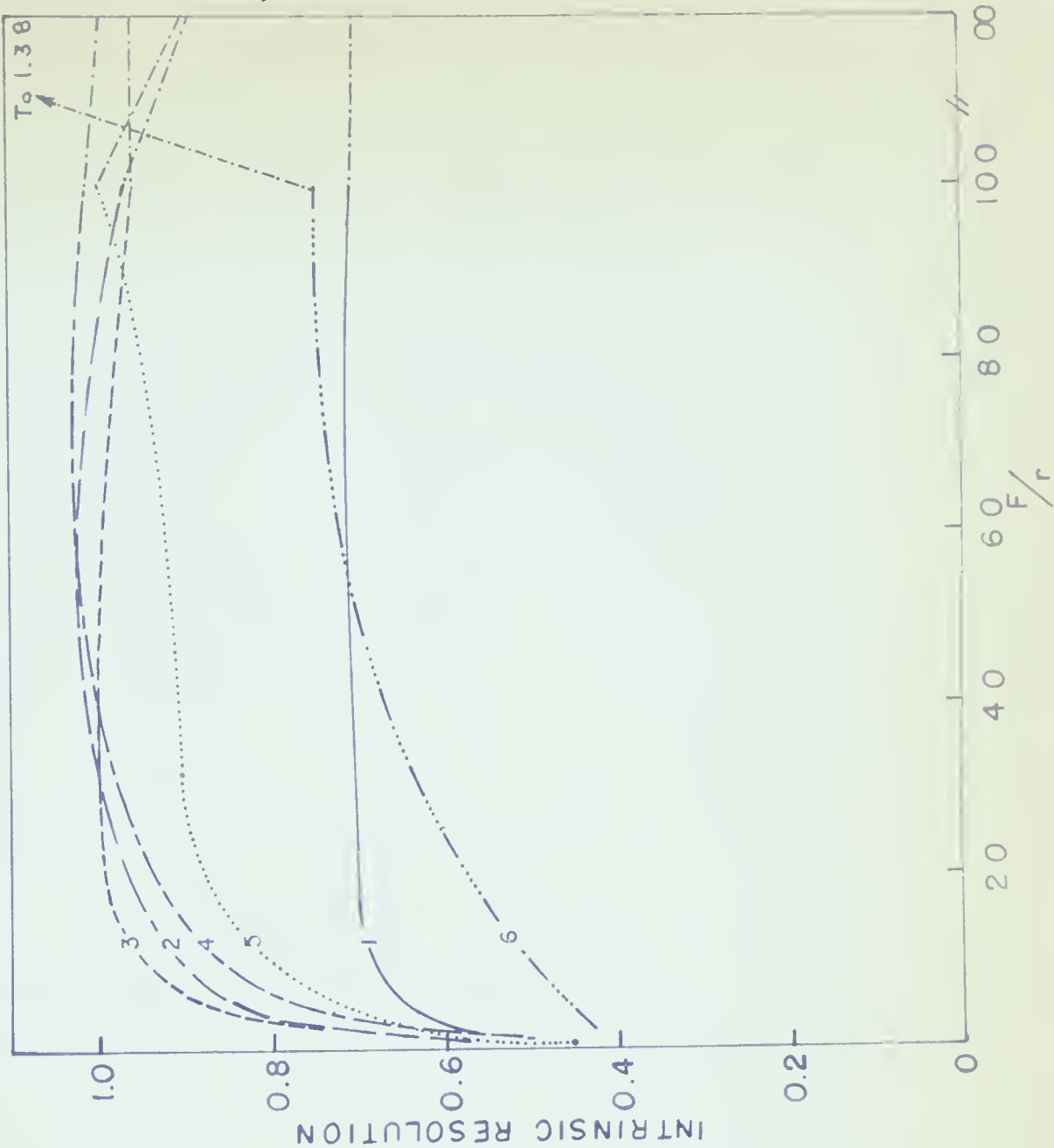
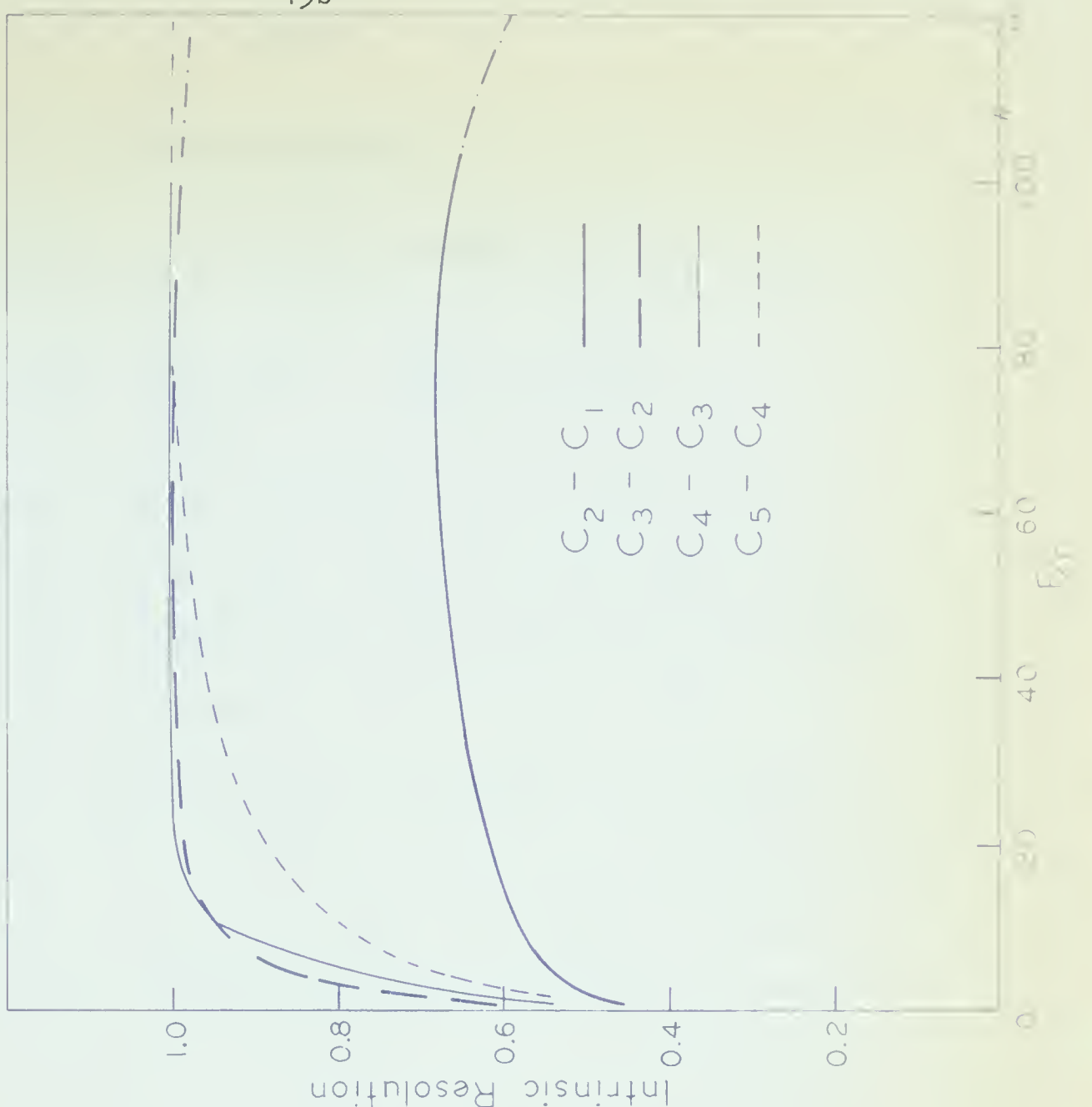
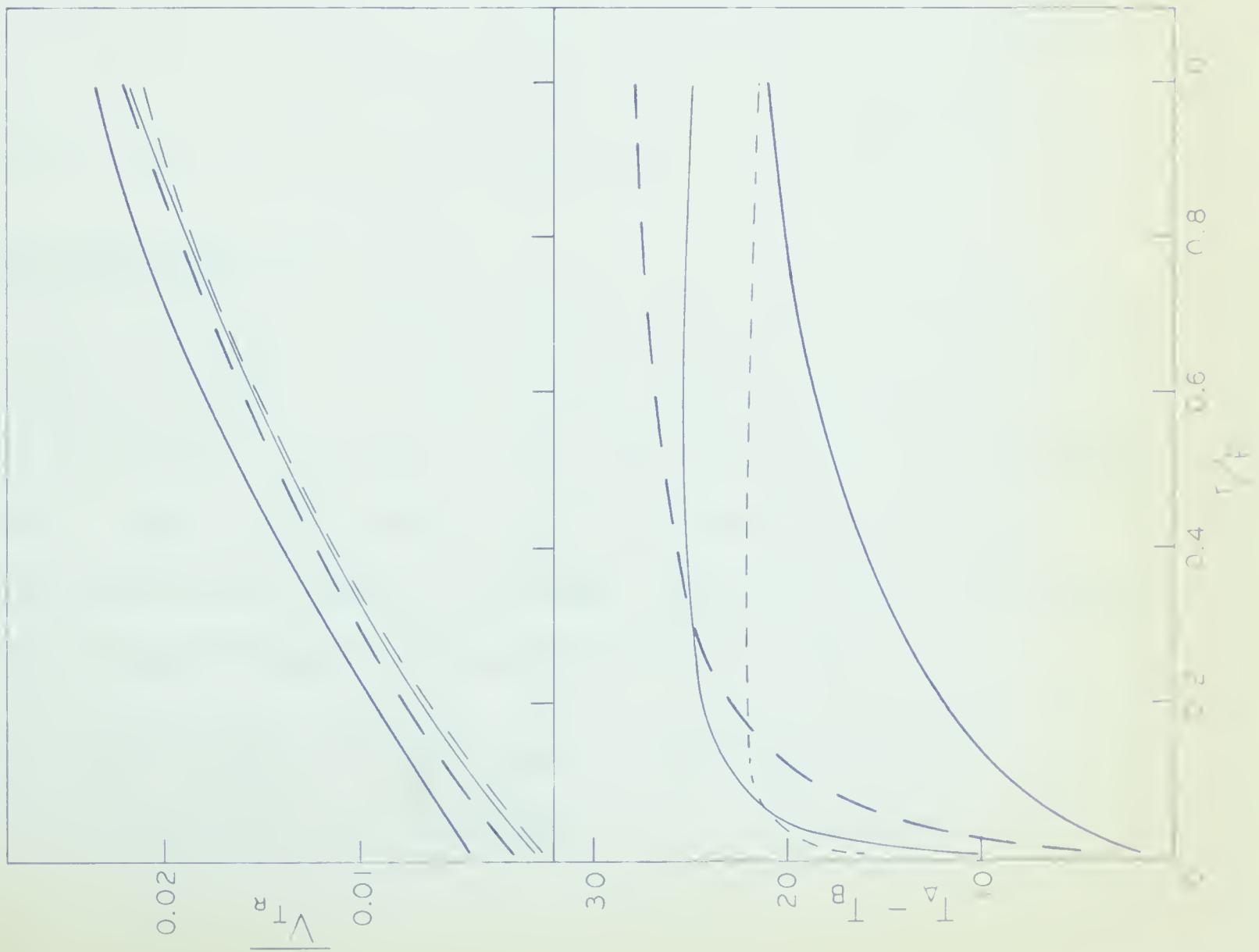


Fig. 15

Values of ΔT and ΔT_{eff} for different values of ΔT and ΔT_{eff} in the case of normal incidence of light on a surface of a medium with refractive index $n = 1.5$.



OVERALL RESOLUTION

As shown earlier the experimentally observed resolution may be expressed as

$$R = \left[\frac{F}{r} \frac{T_A - T_B}{V_{T_R}} \sqrt{\frac{N}{4}} \right] = R_i \sqrt{\frac{N}{4}}$$

Complete prediction involves understanding the factors governing the number of theoretical plates, N . These factors are only qualitatively known at present but since N appears only as the square root, the effect of variation may not be too striking.

The variation of N has already been discussed. N is a maximum at some flow-rate, F , and F , for maximum N , is found to be relatively independent of temperature (27). Figure 3 (in which the inverse of N , H.E.T.P. = L/N has been plotted against temperature) showed that N first increases somewhat and then decreases with increasing temperature, the decrease being usually more significant in the usual temperature range. For the n -hydrocarbon series on Apiezon L, Habgood and Harris have also shown that N increases with carbon number. This was illustrated in Figure 4 where H.E.T.P. has been plotted against carbon number.

Comparison with Experiment

Since retention temperature decreases with increase in F/r , then for any one flow-rate square root N will increase and thus the overall resolution will increase as compared with the steady value reached by intrinsic resolution. Based on this qualitative picture an analysis was made of resolution observed in a number of programmed temperature runs with n -hydrocarbons and aromatic halides. The programs were as follows:

A. $r = 1.6$ deg./min., $F = 44$ ml./min., $F/r = 27.5$ ml./deg.

B. $r = 17$ deg./min., $F = 45$ ml./min., $F/r = 2.6$ ml./deg.

C. $r = 18 \text{ deg./min.}$, $F = 106 \text{ ml./min.}$, $F/r = 6.0 \text{ ml./deg.}$

D. $r = 3.7 \text{ deg./min.}$, $F = 120 \text{ ml./min.}$, $F/r = 32.1 \text{ ml./deg.}$

The flow-rate for maximum N was between 35 and 40 ml./minute. (The chromatograms were obtained in connection with (26)). The results are shown in Table 1.

The theoretical predictions which can be made are:

- (a) F was selected near the optimum 44 and 45 ml./min. and F/r are 27.5 and 2.6 respectively. Resolution in program A should be greater than in program B since the F/r ratio is in the region of high intrinsic resolution in A but not in B. Since the flow-rate is constant the contribution of square root N should be nearly constant.
- (b) F/r was almost constant, 27.5 and 32.4 but F varied, 44 and 120 ml./min. respectively. Resolution in program A should be greater than in program D since both programs are in the region of high intrinsic resolution but the contribution of square root N in D should be less since the flow-rate in D is far above the optimum.

The resolution of the pair n-octane--n-heptane would be expected to be greater than the resolution for the pair n-heptane--n-hexane since N is larger for the higher members of this series.

- (c) F was almost constant, 106 and 120 ml./min. but F/r varied, 6.0 and 32.4 respectively. This situation is similar to (a) except that the relatively constant flow-rate is far above the optimum. Therefore the resolution in program D should be greater than in program C. Thus it can be seen that all observed resolutions fall qualitatively into the predicted pattern.

Optimum Conditions for Maximum Resolution

For optimum overall resolution a flow-rate should be selected which will give close to maximum N. The heating rate may then be set at a max-

imum limited only by the need for keeping within the range for maximum intrinsic resolution (F/r ratio not below 10) in order that the analysis may be carried out in as short a time as is consistent with good resolution. If it is desired to decrease the time of analysis still further, F and r should both be increased to give the minimum sacrifice in resolution.

TABLE 1

Comparison of Resolutions of Some Hydrocarbons
and Aromatic Halides for Various Programs

PROGRAMS				
Program	A	B	C	D
r deg./min.	1.6	17	18	3.7
F ml./min.	44	45	106	120
$(\frac{F}{r})$ ml./deg.	27.5	2.6	6.0	32.4

OBSERVED RESOLUTION

(a) F near optimum, varying F/r

	Resolution		Theoretical Prediction
Program	A	B	
n-heptane - n-hexane	7.4	3.0	A > B

(b) Constant F/r, varying F

	Resolution		Theoretical Prediction
Program	A	D	
m-Br toluene - m-Cl toluene	6.2	5.4	A > D
n-octane - n-heptane	8.0	6.2	A > D
n-heptane - n-hexane	7.4	6.0	A > D

(c) F constant and above optimum, varying F/r

	Resolution		Theoretical Prediction
Program	D	C	
m-Br toluene - m-Cl toluene	5.4	3.2	D > C
n-octane - n-hexane	6.2	3.1	D > C

SUMMARY

1. A brief review of the development of programmed temperature chromatography from conventional isothermal gas chromatography has been made.
2. A review has been made of the contribution to Height Equivalent to a Theoretical Plate of the resistance to mass transfer with particular reference to its variation with temperature and with carbon number in a homologous series.

3. An examination has been made of the relationship of resolution defined as

$$R = \frac{V_B - V_A}{1/2(W_A + W_B)}$$

where V is the retention volume and W the base width for components A and B respectively, to fractional band impurity, which is the fraction of one component contained in ^{the} peak or band of the other component. A graph has been prepared relating these two quantities at various constant values of α , the ratio of retention volumes and of N, the number of theoretical plates.

4. An expression for resolution in programmed temperature gas chromatography has been developed

$$R = \frac{F}{r} \frac{(T_A - T_B)}{V_{T_R}} \sqrt{\frac{N}{4}}$$

which was divided into two parts, the first $\frac{F}{r} \frac{(T_A - T_B)}{V_{T_R}}$, which is dependent on solute-solvent interaction and program has been designated as intrinsic resolution, R_i . The second, $\sqrt{N/4}$, depends only on the number of plates as determined by the actual packing of the column.

5. While the intrinsic resolution for any particular pair of compounds depends only on the program as specified by the ratio of flow-rate to

heating rate and on the starting temperature it was not found possible to find a perfectly general mathematical expression of this relationship. Accordingly, a range of practical situations was examined.

6. In order to choose examples covering all pairs of compounds of practical interest, isothermal retention data which have been reported over a range of temperatures for individual compounds were examined. These may be characterized by the slope and intercept of the $\log V_R - 1/T$ plot, the former being expressed in terms of heat of solution ΔH and the latter being designated as pre-exponential factor, A . It was found that plots of $\log A$ against ΔH fell into a straight line for each homologous series and that all lines were approximately parallel and fell within a narrow band.
7. The relationship of intrinsic resolution, R_i , and its component factors, $T_A - T_B$ and $1/V_{T_R}$ to program and retention characteristics has been examined graphically for a number of hypothetical compounds which covered the range of substances likely to be encountered in practice. The $T_A - T_B$ versus $\frac{r}{F}$ curve for many pairs of compounds has the same general shape. For high starting temperatures $T_A - T_B$ increases approximately linearly with increase in r/F .
The $1/V_{T_R}$ term increases with r/F since retention temperatures are increasing. The rate of increase becomes smaller as the starting temperature of the program is raised. It was found that for most pairs of compounds the curve for the relationship between R_i and F/r was of the same general shape. With increasing F/r a relatively constant value of R_i was reached. The value of F/r for which R_i had reached a relatively constant value varied somewhat from pair to pair of compounds but in general it occurred between 10 and 20.

8. There is little change in R_i throughout the range of F/r examined (1 to 100) for pairs of compounds under certain conditions, namely:
 - (a) relatively high starting temperature (about 20°C in case of compounds having heats of solution of 2,000 to 3,000 and about 200°C in case of compounds with heats of solution 9,000 to 10,000).
 - (b) pairs of compounds with the same heats of solution but different pre-exponential factors.
9. The relationship of intrinsic resolution to program and retention characteristics for pairs of compounds from two homologous series--the n-alcohols and the n-hydrocarbons fell into the pattern set by the typical compounds.
10. The $T_A - T_B$ versus r/F curves indicate that retention temperature is not a linear function of carbon number as has been suggested--since then $T_A - T_B$ would be constant for any given r/F which is not the case except perhaps for $r/F = 0.2$.
11. Qualitative predictions can be made of the variation of observed overall resolution which includes the effect of number of plates. These were tested for a number of actual programs involving normal hydrocarbons and qualitative agreement was found.
12. The conditions for maximum resolution in programmed temperature gas chromatography are:
 - (a) flow-rate near the optimum for maximum N .
 - (b) F/r ratio greater than about 10.
13. In the evaluation of the relation between retention temperature and program, a method for the analytic evaluation of the integral
$$\int_{T_O}^{T_R} \frac{dT}{V_T}$$
has been developed for the case where column dead-space may be neglected.

14. An investigation of effect of column dead-space and of situations where it may be neglected has been made.

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APPENDIX I

Relationship Between Resolution
and Fractional Band Impurity

In gas chromatographic separations, fractional band impurity, which is the fraction of one solute in another on elution from the column, has been defined in a previous section in terms of α , the separation factor. Resolution may be related to the separation factor and hence to the fractional band impurity in the following way:

$$R = \text{resolution} = V_A - V_B / \Delta V_{\text{ave}}.$$

$$\alpha = \text{separation factor} = V_A / V_B$$

From the definition of N

$$V_A / \Delta V_{\text{ave}} = \sqrt{N}/4$$

thus

$$\begin{aligned} R &= V_A(\alpha - 1) / \Delta V_{\text{ave}} \\ &= \sqrt{N}(\alpha - 1) / 4 \end{aligned}$$

If N is held constant, then R may be calculated for various values of α and the fractional band impurity, η , may be read from Glueckauf's (18) plots relating number of plates, separation factor and fraction band impurity.

The relation between fractional band impurity and resolution is shown in Figure 20 for a number of values of N. Lines of constant α are also shown.

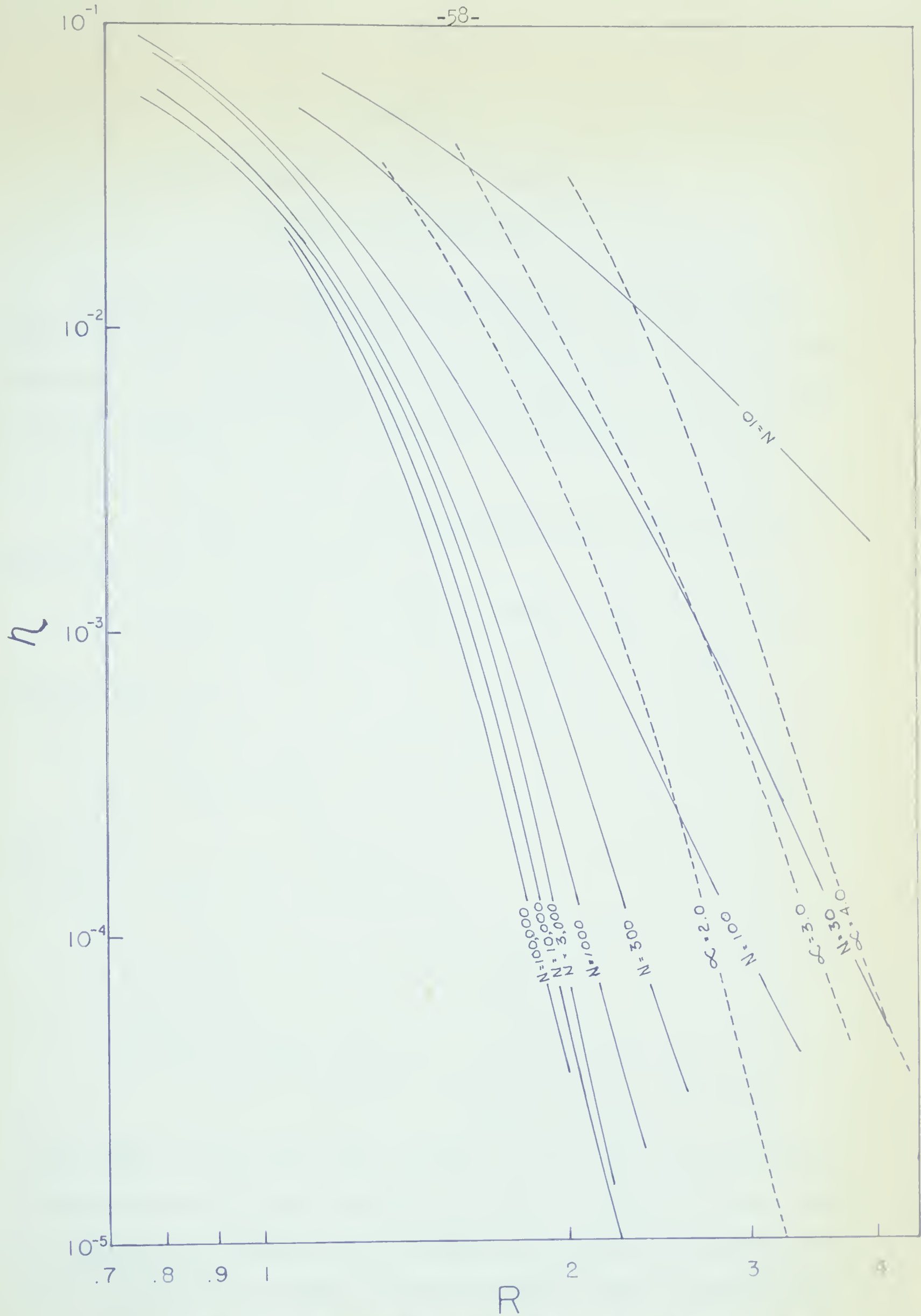


Fig.

Relation of fractional beam impurity, η , to resolution, R , for various constant values, N , and for various constant values of α (2.0, 3.0, 4.0).

APPENDIX II

Analytical Evaluation of the Relation of r/F and Retention Temperature

Since, as will be shown empirically in Appendix III, for solutes appreciably removed from the air peak, the relation of r/F versus retention temperature is not greatly affected by substituting the net retention volume for V_T , the integral $\int_{T_0}^{T_R} \frac{dT}{V_T}$ was analytically evaluated as follows:

$$V_T = A \exp. (\Delta H/RT) (\text{neglecting column dead-space}) \quad (1)$$

Substituting in the integral gives

$$r/F = \int_{T_0}^{T_R} \frac{1}{A \exp.(-\Delta H/RT)} dT \quad (2)$$

to change variables:

$$\text{Let } X = \Delta H/RT \quad (3)$$

$$dT = (-\Delta H/RX^2) dX \quad (4)$$

(1) now becomes

$$\begin{aligned} r/F &= -\Delta H/RA \int_{X_0}^{X_R} (e^{-X}/X^2) dX \\ &= -\Delta H/RA \left[(-e^{-X}/X) - \int (e^{-X}/X) dX \right]_{X_0}^{X_R} \\ &= \Delta H/RA \left[\left(e^{-X_R}/X_R \right) - \left(e^{-X_0}/X_0 \right) + \int_{X_0}^{X_R} (e^{-X}/X) dX - \int_{X_R}^{\infty} (e^{-X}/X) dX \right] \quad (5) \end{aligned}$$

The value of the exponential integral $\int (e^{-X}/X) dX$ has been tabulated for various values of X and, therefore, equation (5) can be evaluated. However, at present the tabulated values extend only to $X = 15$ and therefore, for a starting temperature of roughly 300°K the integral cannot be evaluated for heats of solution higher than 9,000 calories per mole. In view of the fact that tables of exponential integrals are inadequate, and also that in most

cases numerical integration was found to be faster, most of the calculations for this thesis were done by numerical integration.

APPENDIX IIISignificance of Column Dead-space in Calculation of Retention
Temperatures and Intrinsic Resolution.

The calculation of the relationship of r/F to temperature is very much simplified if the contribution of column dead-space to isothermal retention volume may be ignored. Also many isothermal retention data are quoted without giving details of column length or dead-space. Therefore, a comparison was made between values obtained when dead-space was included in the calculation and when it was excluded.

The contribution of dead-space volume is important both directly in the calculation of the curves relating retention temperatures and r/F , and in the calculation of resolution which depends on these curves. However, since $T_A - T_B$ is a factor rather than temperature directly, the net effect on resolution is difficult to estimate.

Giddings (15) has suggested that in estimating retention temperature the dead-space may safely be ignored for all cases of practical interest. One would expect this to be true for compounds with retention volumes much greater than air. Figure 25, Curves 4, 6 and 7 show that the contribution of column dead-space to the calculation of retention temperature is not negligible for all compounds. Curves 8 and 9 indicate that for compounds with high heats of solution at a low starting temperature, the contribution of column dead-space may be ignored.

An examination of the contribution of dead-space to retention temperature and to intrinsic resolution was made for two pairs of compounds. One of the pairs of compounds had relatively high heats of solution and the other pair relatively low. The retention characteristics of compounds with high heats of solution at high starting temperatures would be expected to

be similar to the retention characteristics of compounds with low heats of solution at relatively low starting temperatures. Therefore, these two situations were examined. For the pair of compounds characterized by $10^{-3.5}$ 10,000 and 10^{-3} 9,000 which are similar to successive members of a homologous series, at a starting temperature of 20°C, Figure 21 shows that the intrinsic resolution versus F/r curve obtained by ignoring the dead-space is the same as the intrinsic resolution versus F/r curve where the dead-space has been included in the calculation. However, for a second pair of compounds characterized by 10^{-1} 2,000 and $10^{-1.3}$ 3,000¹⁷ at a starting temperature of 20°C, Figure 22 of $T_A - T_B$, $1/V_{T_R}$ and intrinsic resolution shows that the dead-space may not be ignored, since the retention volume is not large in comparison with dead-space volume ($V_T/V_{d.s.} < 40$). The usual situation is that the column dead-space may be ignored since the great majority of compounds will have retention volumes much larger than the dead-space volume.

A further examination was made of these two pairs of compounds for programs where the integrals have been calculated from a starting temperature of absolute zero to higher temperatures in the case of the compounds with the low heats of solution and from 200°C for the compounds with the higher heats of solution. Plots of intrinsic resolution and the factors thereof are shown in Figures 23 and 24. The intrinsic resolution of the pair of compounds represented by $\Delta H = 9,000$ and 10,000 is then dependent on whether or not the column dead-space has been included in the calculation. For the pair of compounds represented by $\Delta H = 2,000$ and 3,000, the contribution of column dead-space to retention temperatures and to intrinsic resolution is still not negligible. Therefore, column dead-space may never be ignored when dealing with compounds which have low heats of solution.

The retention temperature where column dead-space is included may be calculated from the retention temperature where dead-space has been excluded, in certain cases. In Figure 25 the retention temperature differences, $T_R - T_R'$ (where T_R and T_R' have been calculated including and excluding, respectively, the column dead-space) is plotted against r/F . For comparative purposes the difference between the starting temperature and the retention temperature of air (assuming no absorption of air in the liquid phase) has been plotted against r/F . It is seen that for comparatively high starting temperatures, (e.g. $T_0 = 20^\circ\text{C}$ for low ΔH compounds) the retention temperature can be calculated by adding to the value obtained when dead-space has been ignored, the difference between the starting temperature and the retention temperature for air.

Fig. 11

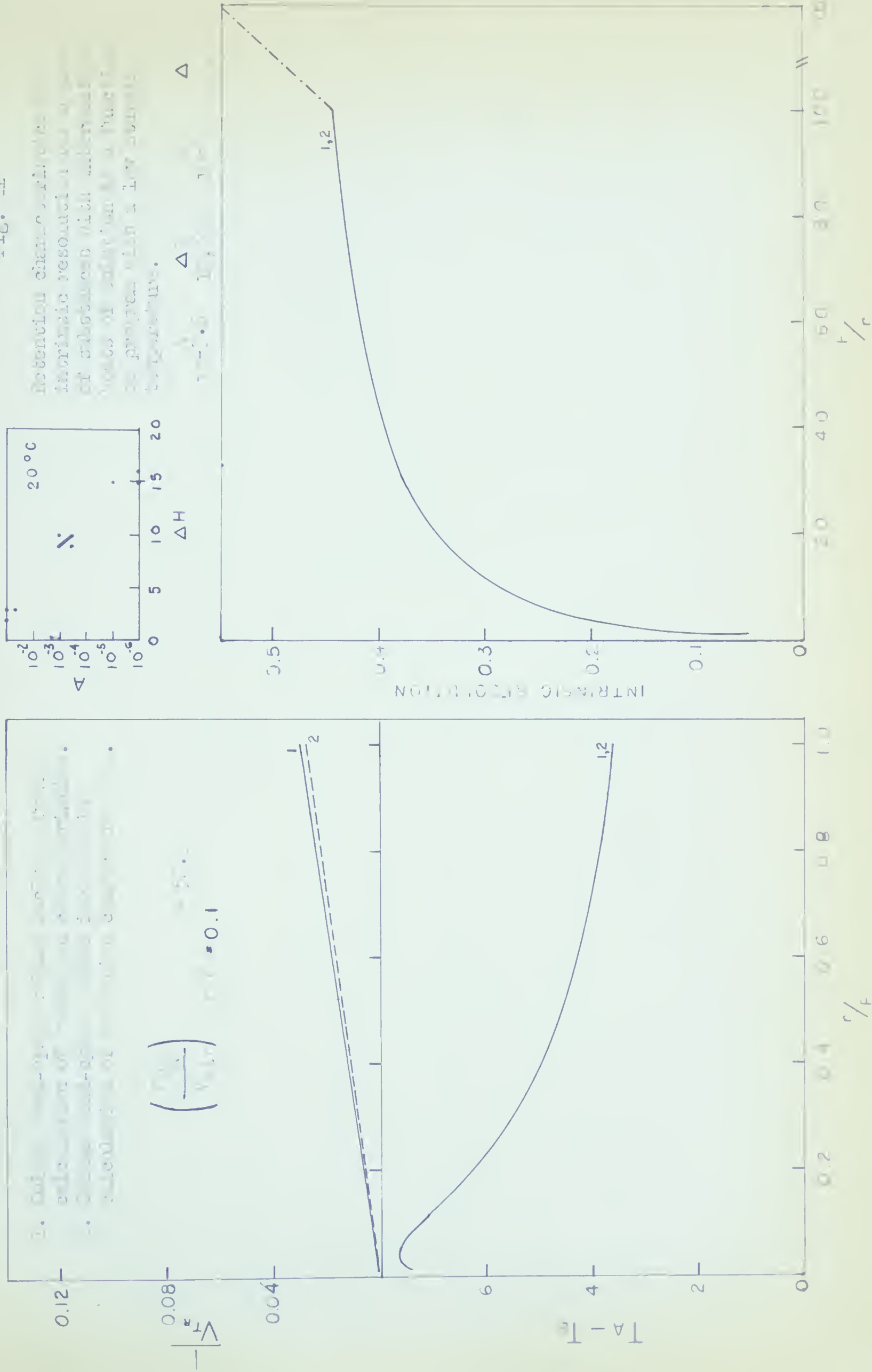
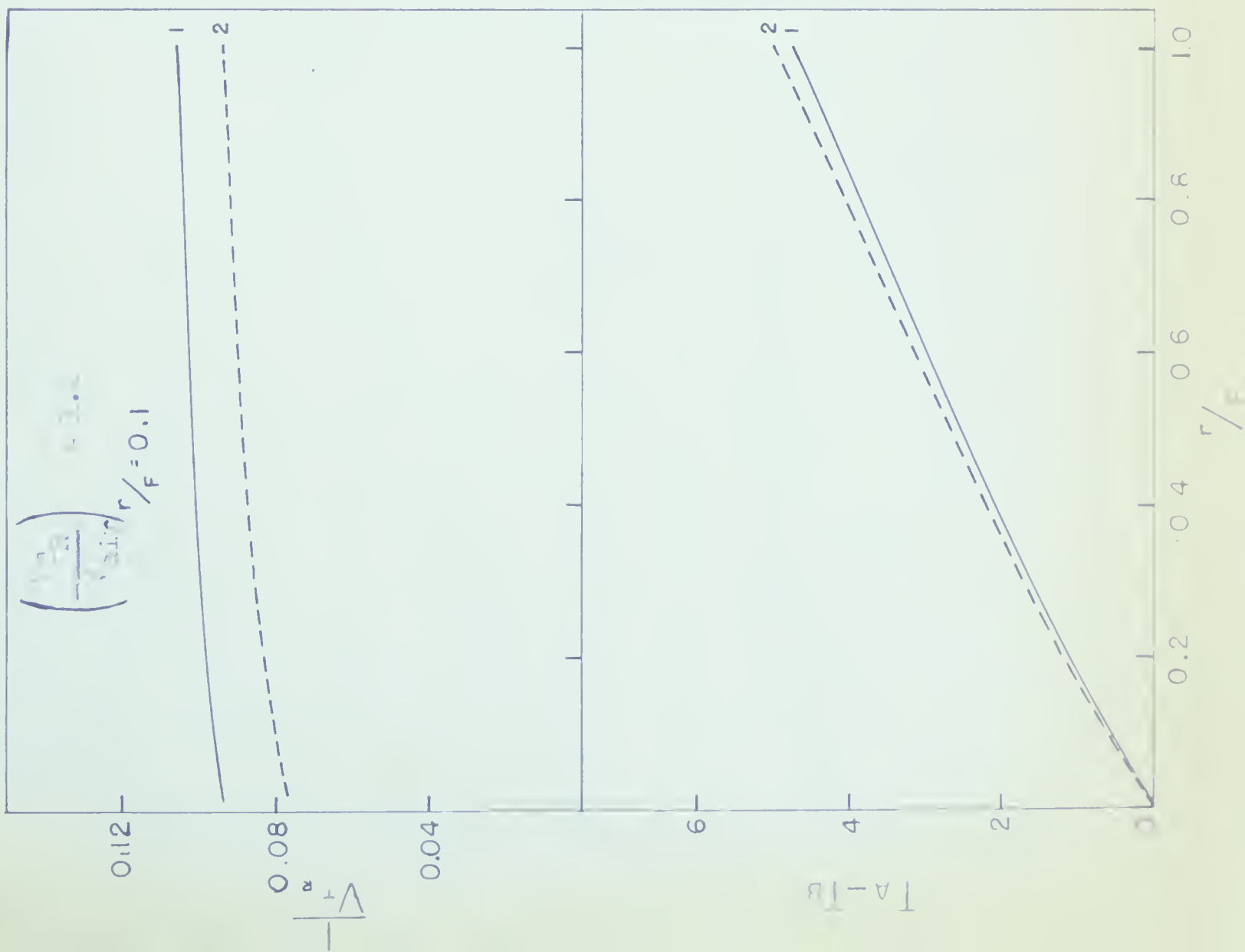
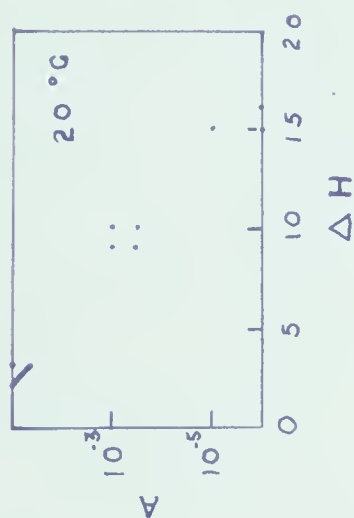


Fig. 22



... high starting temperature.

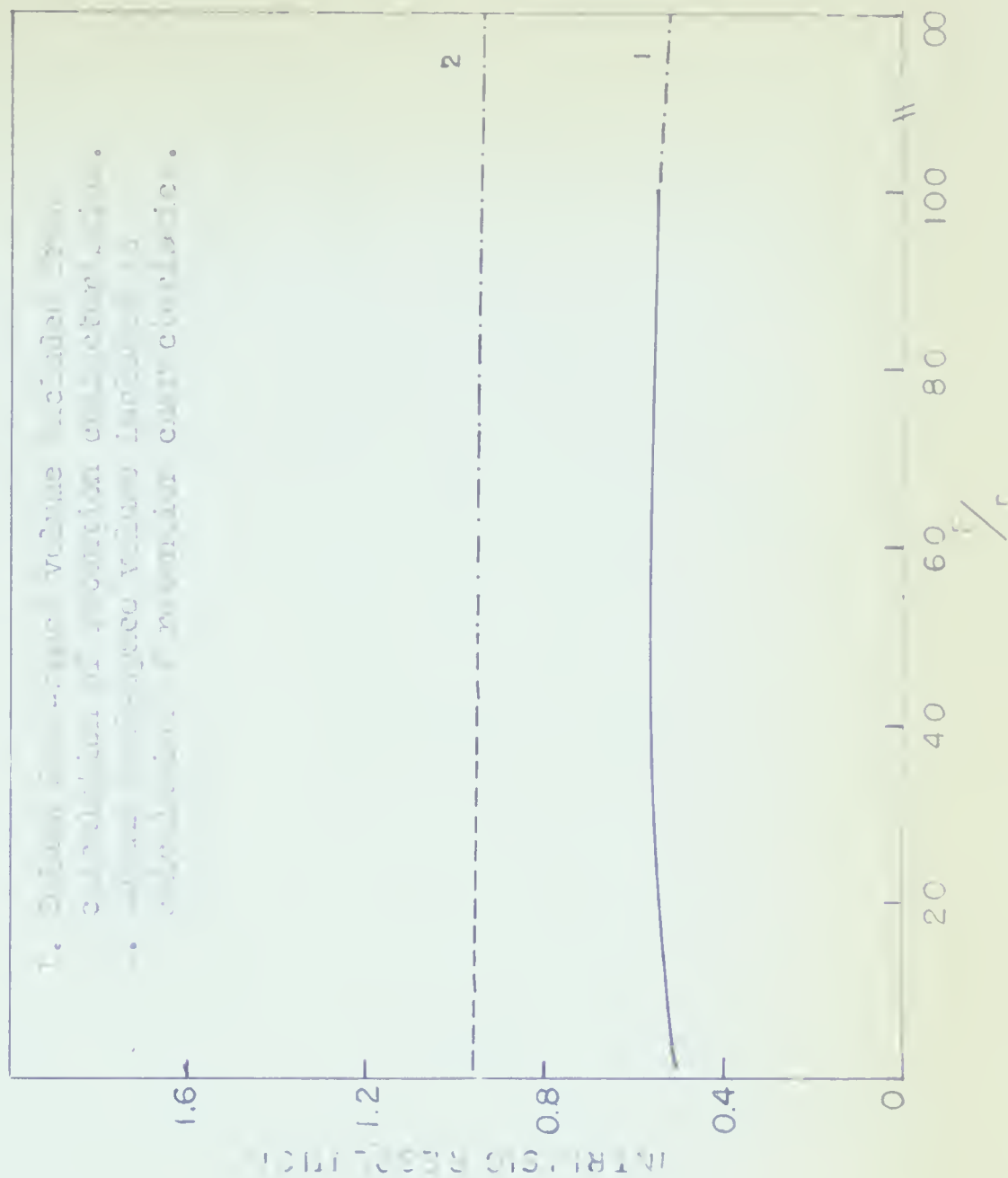
Δ

Δ

0.3

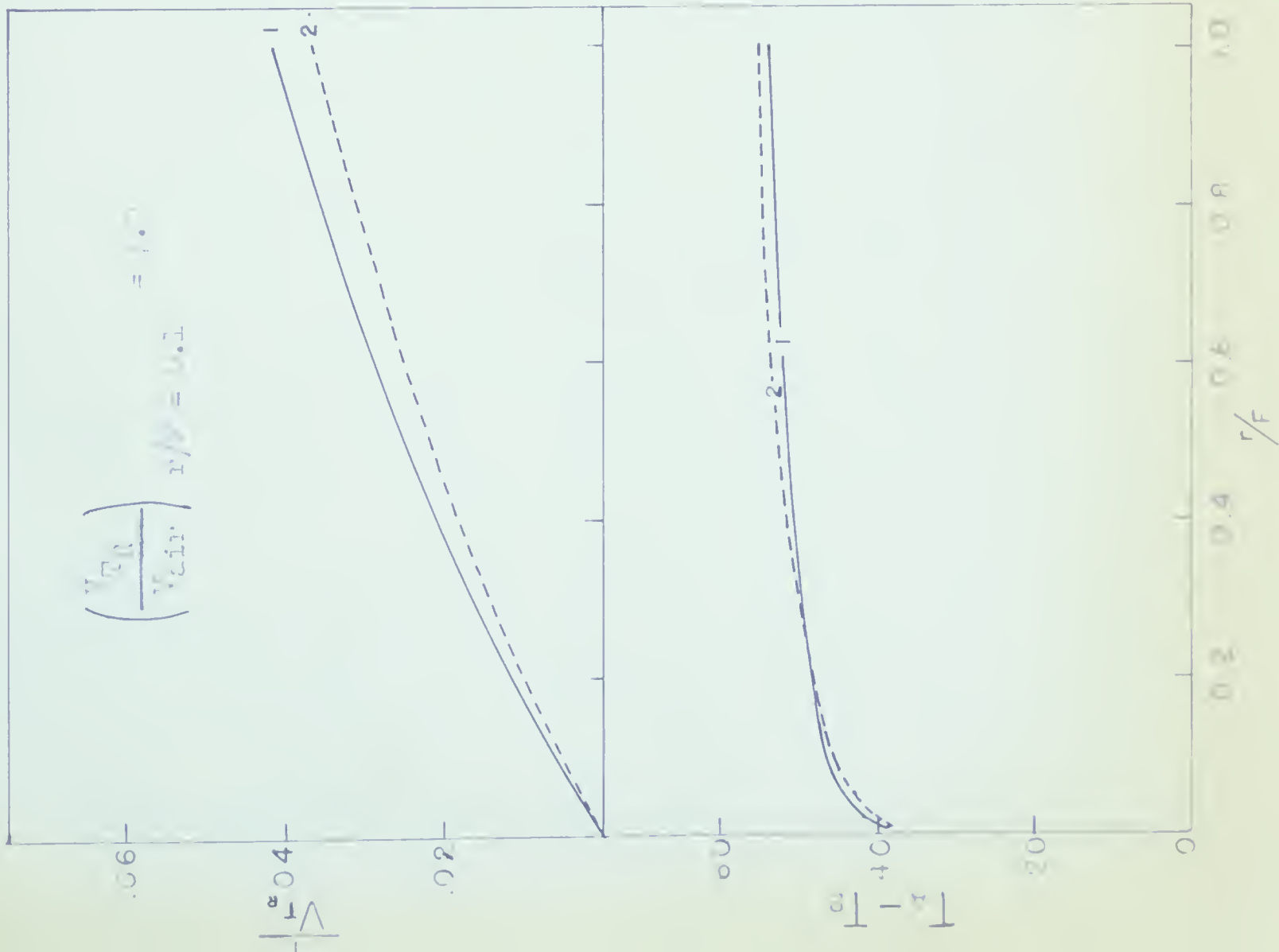
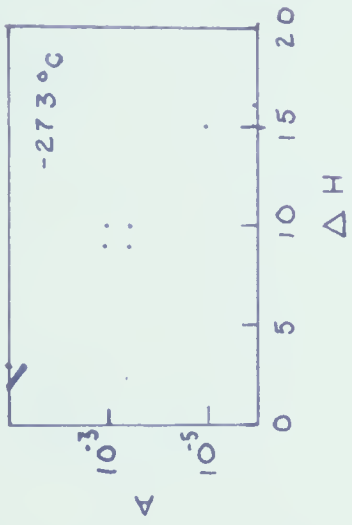
Δ

0.3



1. ... value ...
2. ... value ...

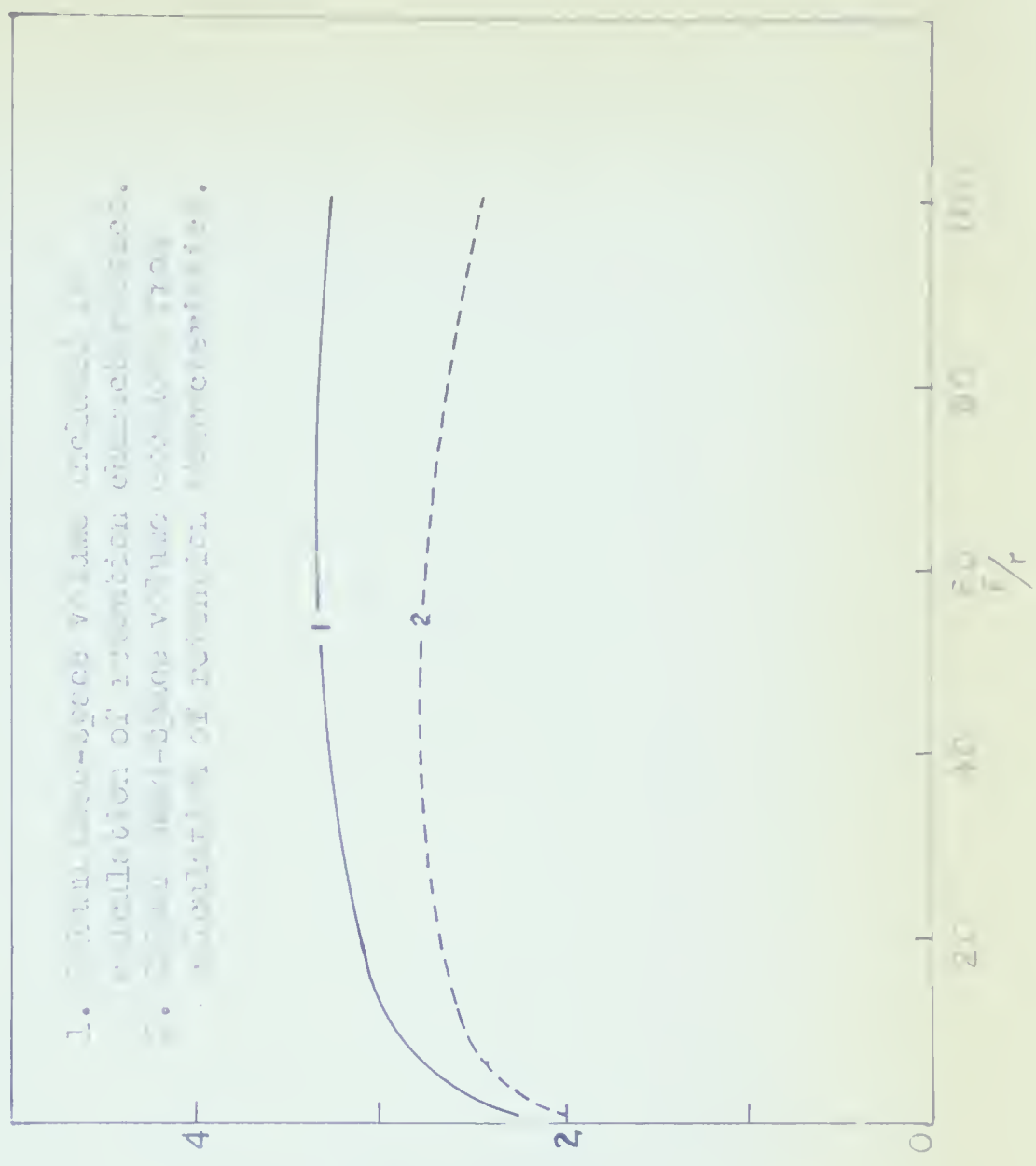
Fig. 80



Received characteristic
intrinsic permeability
states with low levels of
solution as a function of
from area of low per-
structure.

ΔC Δ Δ

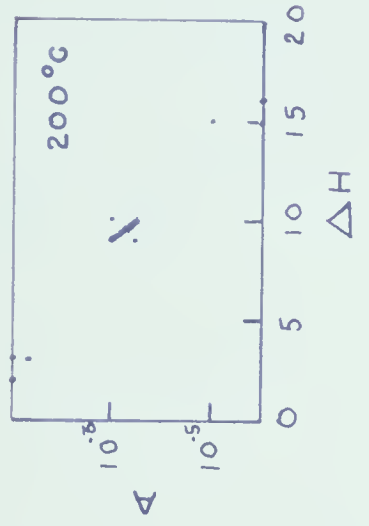
-1.0 1.0 2.0



1. Normalized volume calculated as a function of position of permeability.
2. Normalized volume calculated as a function of position of permeability.

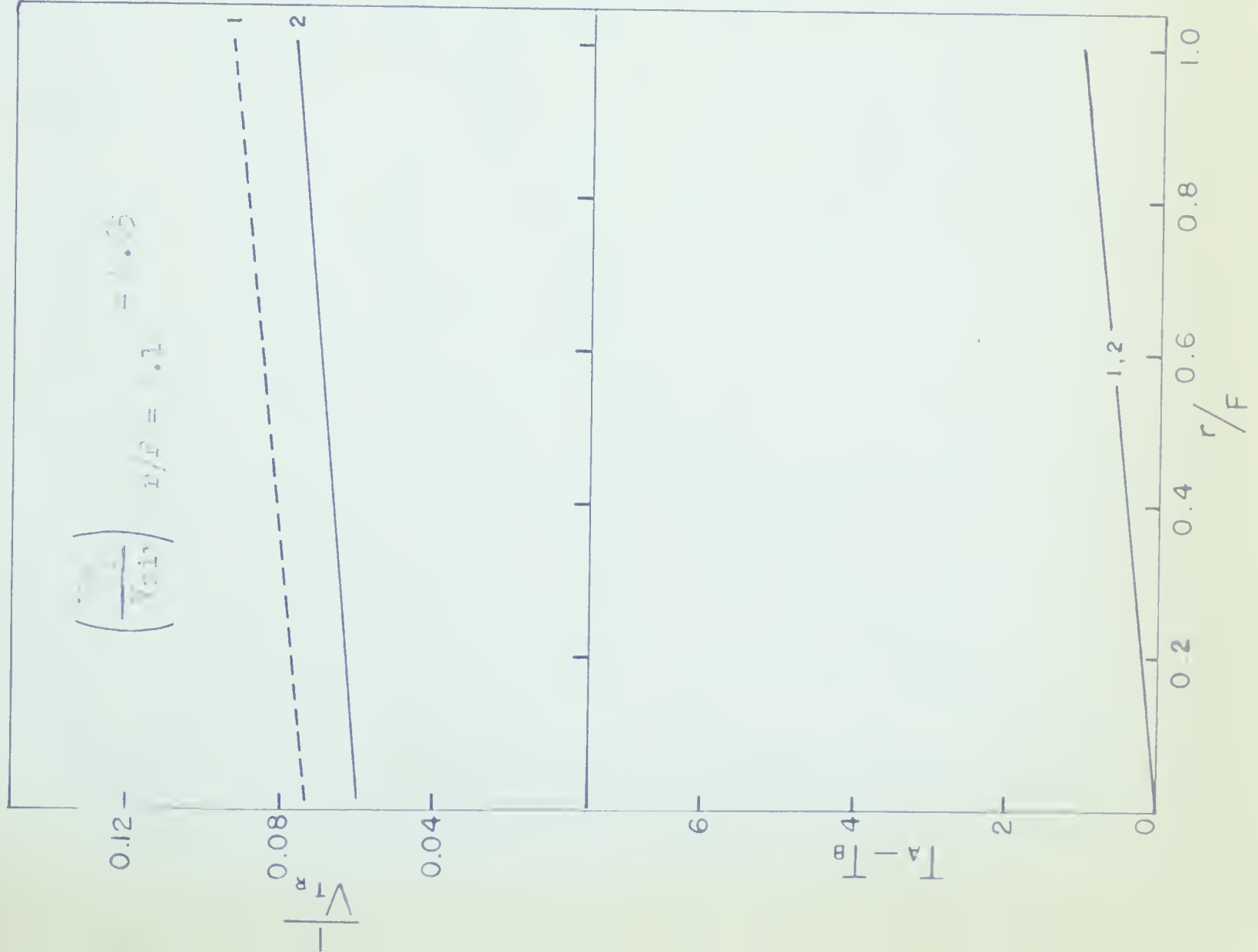
Fig. 24

Retention characteristics
intrinsic resolution for a pair
of substances with intermediate
heats of solution as a function
of program with a high starting
temperature.



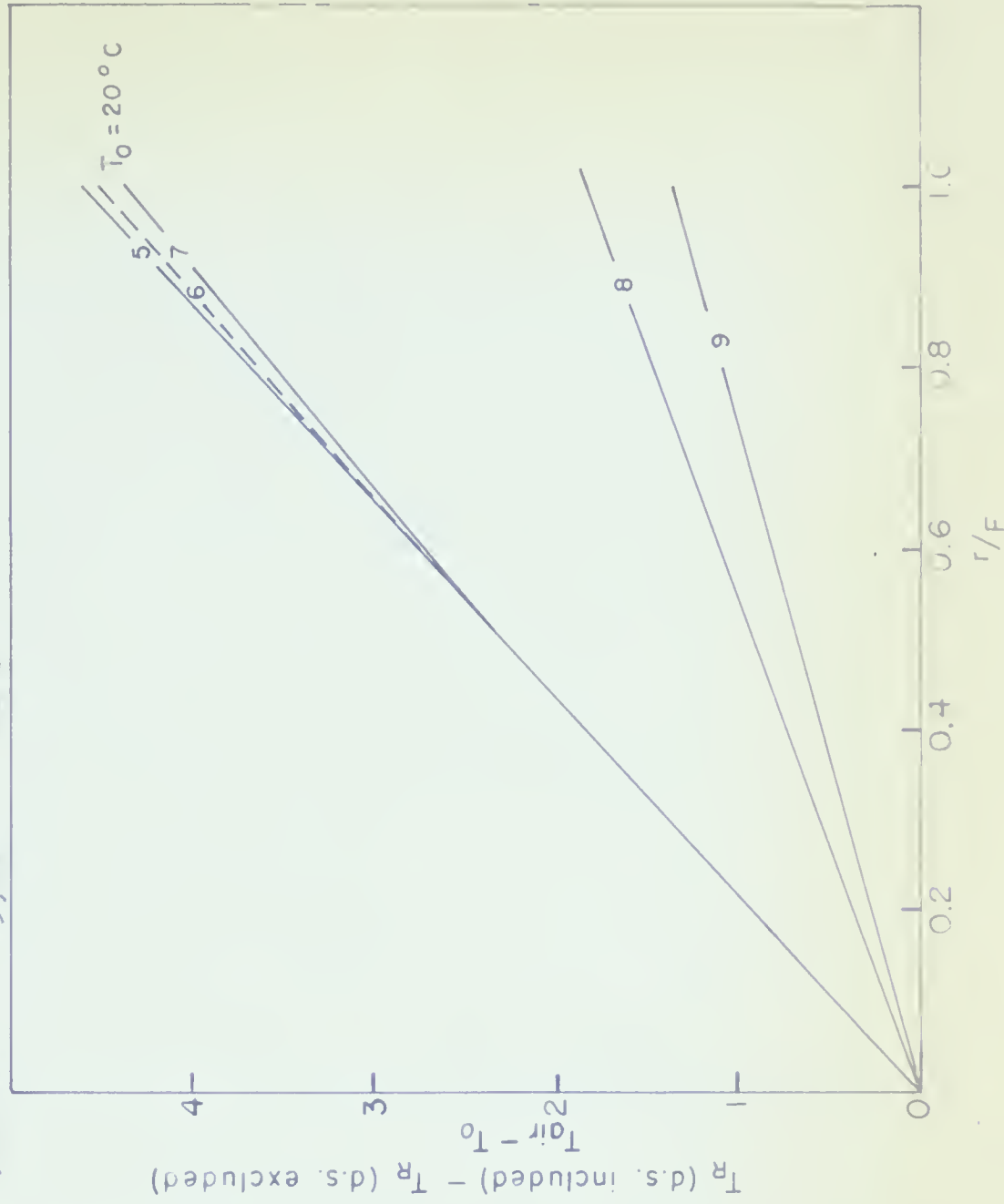
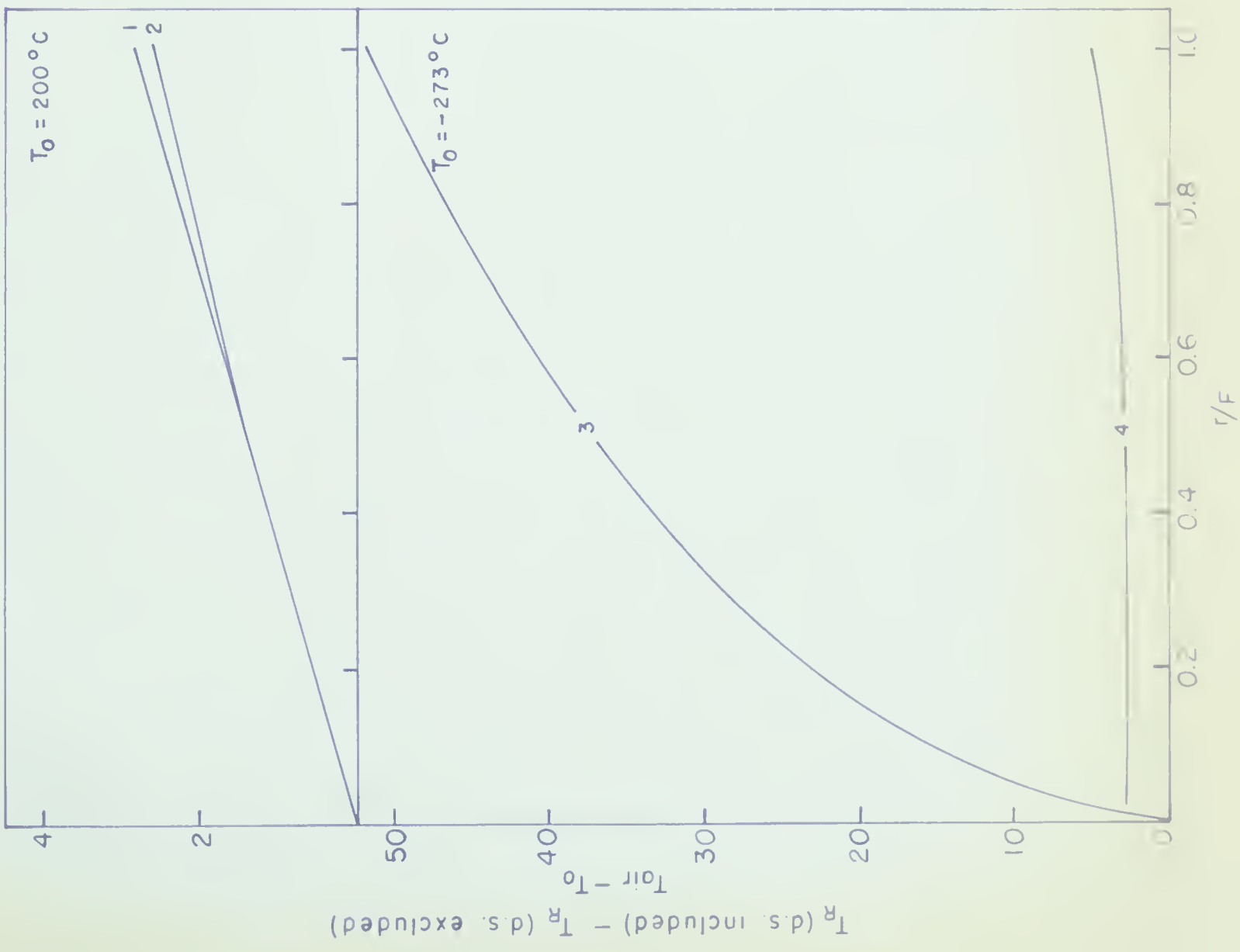
ΔH

10^{-5} 10^{-6}



1. Column temperature values excluded from calculation of retention characteristics.
2. Column temperature values included in calculation of retention characteristics.

A	ΔT	T_0
1. Air	0	200°C
2. 10-100	10, 100	200°C
3. 10-100	10, 100	100°C
4. Air	0	100°C
5. 10-100	10, 100	100°C
6. 10-100	10, 100	100°C
7. Air	0	100°C
8. 10-100	10, 100	100°C
9. 10-100	10, 100	100°C
10. Air	0	100°C
11. 10-100	10, 100	100°C
12. 10-100	10, 100	100°C
13. Air	0	100°C
14. 10-100	10, 100	100°C
15. 10-100	10, 100	100°C
16. Air	0	100°C
17. 10-100	10, 100	100°C
18. 10-100	10, 100	100°C
19. Air	0	100°C
20. 10-100	10, 100	100°C
21. 10-100	10, 100	100°C
22. Air	0	100°C
23. 10-100	10, 100	100°C
24. 10-100	10, 100	100°C
25. Air	0	100°C
26. 10-100	10, 100	100°C
27. 10-100	10, 100	100°C
28. Air	0	100°C
29. 10-100	10, 100	100°C
30. 10-100	10, 100	100°C
31. Air	0	100°C
32. 10-100	10, 100	100°C
33. 10-100	10, 100	100°C
34. Air	0	100°C
35. 10-100	10, 100	100°C
36. 10-100	10, 100	100°C
37. Air	0	100°C
38. 10-100	10, 100	100°C
39. 10-100	10, 100	100°C
40. Air	0	100°C
41. 10-100	10, 100	100°C
42. 10-100	10, 100	100°C
43. Air	0	100°C
44. 10-100	10, 100	100°C
45. 10-100	10, 100	100°C
46. Air	0	100°C
47. 10-100	10, 100	100°C
48. 10-100	10, 100	100°C
49. Air	0	100°C
50. 10-100	10, 100	100°C
51. 10-100	10, 100	100°C
52. Air	0	100°C
53. 10-100	10, 100	100°C
54. 10-100	10, 100	100°C
55. Air	0	100°C
56. 10-100	10, 100	100°C
57. 10-100	10, 100	100°C
58. Air	0	100°C
59. 10-100	10, 100	100°C
60. 10-100	10, 100	100°C
61. Air	0	100°C
62. 10-100	10, 100	100°C
63. 10-100	10, 100	100°C
64. Air	0	100°C
65. 10-100	10, 100	100°C
66. 10-100	10, 100	100°C
67. Air	0	100°C
68. 10-100	10, 100	100°C
69. 10-100	10, 100	100°C
70. Air	0	100°C
71. 10-100	10, 100	100°C
72. 10-100	10, 100	100°C
73. Air	0	100°C
74. 10-100	10, 100	100°C
75. 10-100	10, 100	100°C
76. Air	0	100°C
77. 10-100	10, 100	100°C
78. 10-100	10, 100	100°C
79. Air	0	100°C
80. 10-100	10, 100	100°C
81. 10-100	10, 100	100°C
82. Air	0	100°C
83. 10-100	10, 100	100°C
84. 10-100	10, 100	100°C
85. Air	0	100°C
86. 10-100	10, 100	100°C
87. 10-100	10, 100	100°C
88. Air	0	100°C
89. 10-100	10, 100	100°C
90. 10-100	10, 100	100°C
91. Air	0	100°C
92. 10-100	10, 100	100°C
93. 10-100	10, 100	100°C
94. Air	0	100°C
95. 10-100	10, 100	100°C
96. 10-100	10, 100	100°C
97. Air	0	100°C
98. 10-100	10, 100	100°C
99. 10-100	10, 100	100°C
100. Air	0	100°C



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